



US010797318B2

(12) **United States Patent**
Sun et al.

(10) **Patent No.:** **US 10,797,318 B2**
(45) **Date of Patent:** **Oct. 6, 2020**

(54) **POSITIVE ELECTRODE ACTIVE MATERIAL, METHOD FOR MANUFACTURING SAME, AND LITHIUM SECONDARY BATTERY CONTAINING SAME**

(71) Applicant: **IUCF-HYU (INDUSTRY-UNIVERSITY COOPERATION FOUNDATION HANYANG UNIVERSITY)**, Seoul (KR)

(72) Inventors: **Yang-Kook Sun**, Seoul (KR); **Gang-Jun Park**, Seoul (KR); **Un Hyuck Kim**, Gunpo-si (KR)

(73) Assignee: **IUCF-HYU (INDUSTRY-UNIVERSITY COOPERATION FOUNDATION HANYANG UNIVERSITY)**, Seoul (KR)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **16/155,232**

(22) Filed: **Oct. 9, 2018**

(65) **Prior Publication Data**
US 2019/0044142 A1 Feb. 7, 2019

Related U.S. Application Data

(63) Continuation of application No. PCT/KR2017/002698, filed on Mar. 13, 2017.

(30) **Foreign Application Priority Data**

Apr. 8, 2016 (KR) 10-2016-0043718
Feb. 17, 2017 (KR) 10-2017-0021894

(51) **Int. Cl.**
H01M 4/525 (2010.01)
H01M 4/505 (2010.01)
H01M 4/04 (2006.01)
H01M 10/052 (2010.01)

(Continued)

(52) **U.S. Cl.**
CPC **H01M 4/525** (2013.01); **C01G 53/04** (2013.01); **C01G 53/42** (2013.01); **H01M 4/366** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC H01M 10/052; H01M 4/366; H01M 4/485; H01M 4/505; H01M 4/525; H01M 4/626
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

9,608,266 B2* 3/2017 Paulsen C01G 53/50
2013/0089787 A1 4/2013 Nagai
(Continued)

FOREIGN PATENT DOCUMENTS

CN 105378985 A 3/2016
EP 1 321 994 A2 6/2003
(Continued)

OTHER PUBLICATIONS

Sung-Kyun Jung et al., "Understanding the Degradation Mechanisms of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Cathode Material in Lithium Ion Batteries", *Advanced Energy Materials*, 2014, 7 pages, vol. 4, No. 1300787.

(Continued)

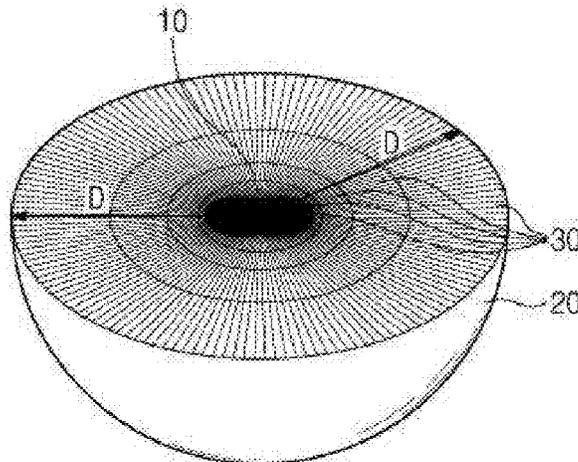
Primary Examiner — Robert S Jones
Assistant Examiner — Rachel L Zhang

(74) *Attorney, Agent, or Firm* — Sughrue Mion, PLLC

(57) **ABSTRACT**

A positive active material is provided. The positive active material may include lithium, an additive metal, and at least one of nickel, cobalt, manganese, or aluminum. The additive metal may include an element different from nickel, cobalt, manganese, and aluminum, and an average content of the additive metal may be less than 2 mol %.

11 Claims, 38 Drawing Sheets



- | | | | | | |
|------|-------------------|-----------|------------------|--------|--------------------------|
| (51) | Int. Cl. | | 2015/0228974 A1 | 8/2015 | Kokado et al. |
| | C01G 53/00 | (2006.01) | 2016/0079595 A1 | 3/2016 | Sun et al. |
| | H01M 4/485 | (2010.01) | 2016/0099469 A1* | 4/2016 | Paulsen C01G 53/50 |
| | C01G 53/04 | (2006.01) | | | 429/223 |
| | H01M 4/62 | (2006.01) | | | |
| | H01M 4/36 | (2006.01) | | | |
| | H01M 4/02 | (2006.01) | | | |

FOREIGN PATENT DOCUMENTS

- | | | | | | |
|------|-----------------|--|----|-------------------|---------|
| (52) | U.S. Cl. | | EP | 2 752 923 A1 | 7/2014 |
| | CPC | H01M 4/485 (2013.01); H01M 4/505 | EP | 3 007 253 A1 | 4/2016 |
| | | (2013.01); H01M 4/626 (2013.01); H01M | JP | 2006-236762 A | 9/2006 |
| | | 10/052 (2013.01); C01P 2002/52 (2013.01); | KR | 10-2010-0042145 A | 4/2010 |
| | | C01P 2002/54 (2013.01); C01P 2002/72 | KR | 10-2011-0099935 A | 9/2011 |
| | | (2013.01); C01P 2004/03 (2013.01); C01P | KR | 10-2012-0030632 A | 3/2012 |
| | | 2004/04 (2013.01); C01P 2004/12 (2013.01); | KR | 10-1400593 B1 | 5/2014 |
| | | C01P 2004/45 (2013.01); H01M 4/0471 | KR | 10-2014-0142171 A | 12/2014 |
| | | (2013.01); H01M 2004/021 (2013.01); H01M | KR | 10-2016-0023496 A | 3/2016 |
| | | 2004/028 (2013.01) | | | |

(56) **References Cited**

U.S. PATENT DOCUMENTS

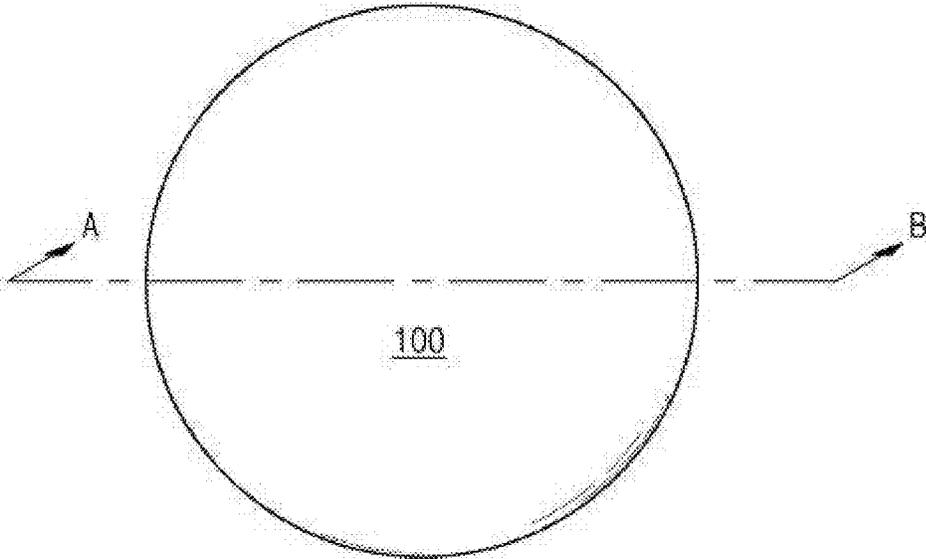
- | | | | |
|------------------|--------|--------------|-----------|
| 2014/0158932 A1* | 6/2014 | Sun | H01M 4/13 |
| | | | 252/182.1 |
| 2014/0205901 A1 | 7/2014 | Nagai et al. | |

OTHER PUBLICATIONS

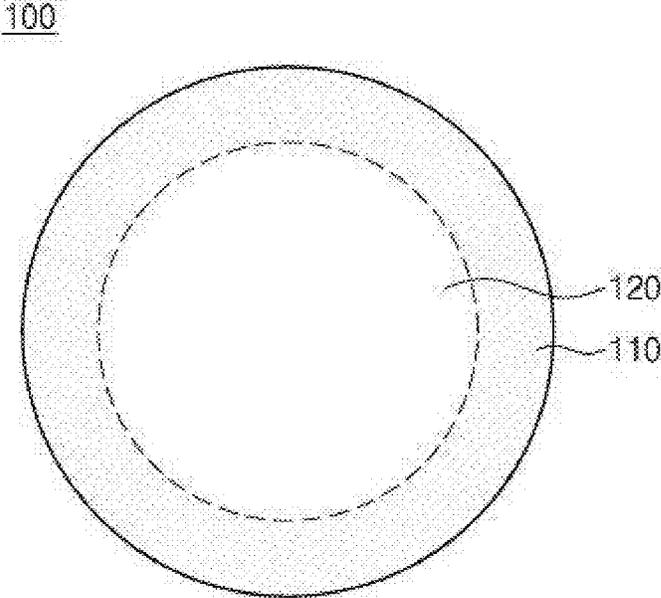
International Search Report for PCT/KR2017/002698 dated Jun. 19, 2017 [PCT/ISA/210].

* cited by examiner

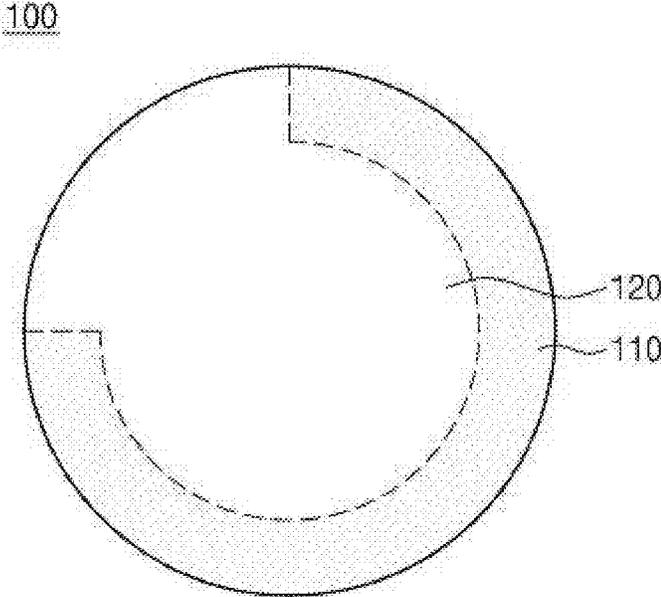
【Fig. 1】



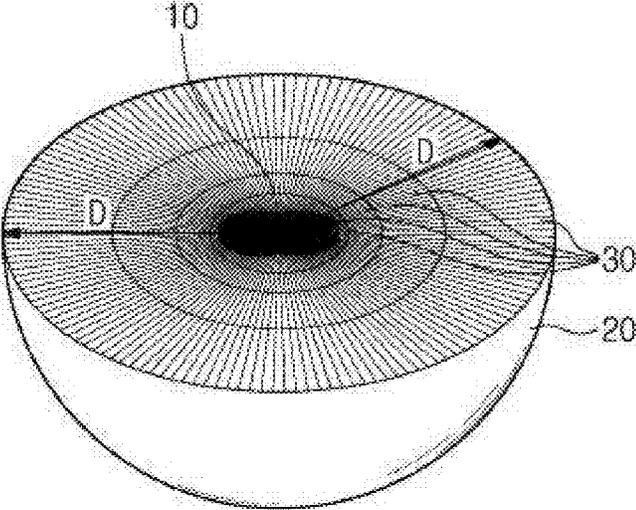
【Fig. 2】



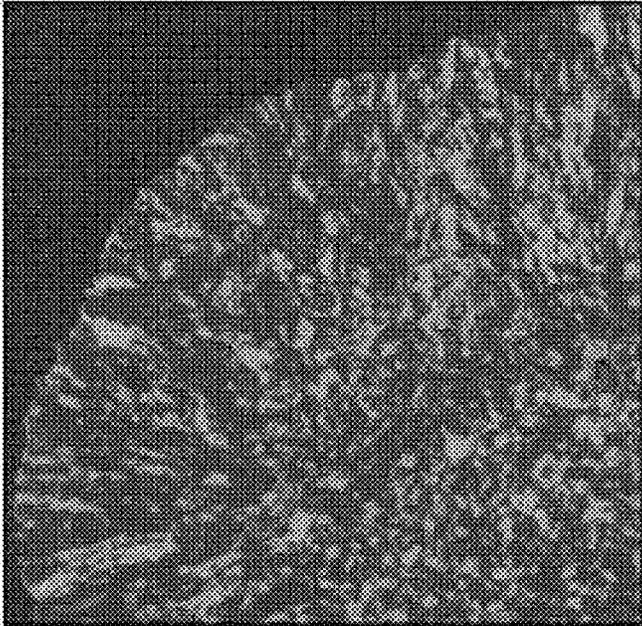
【Fig. 3】



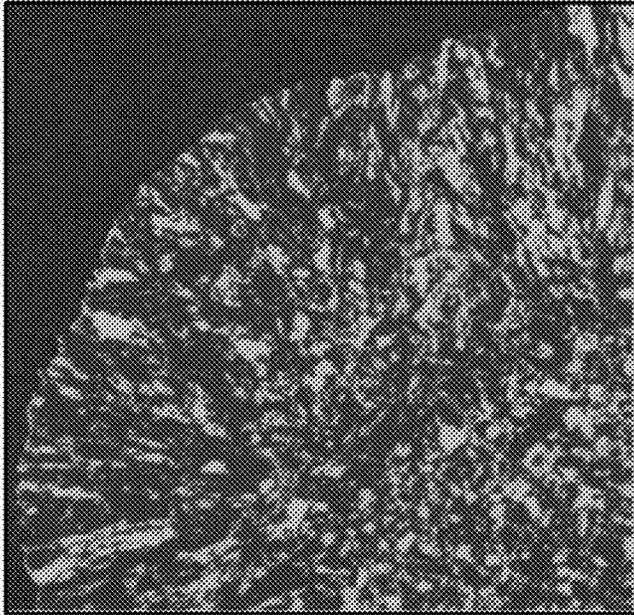
【Fig. 4】



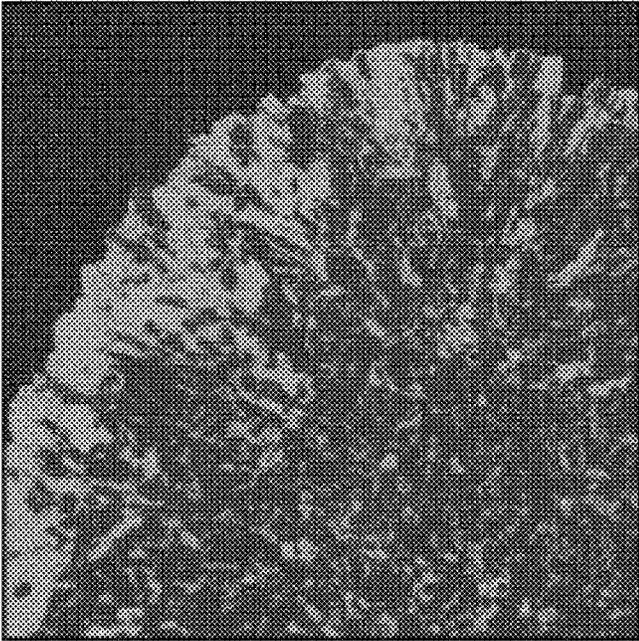
【Fig. 5(a)】



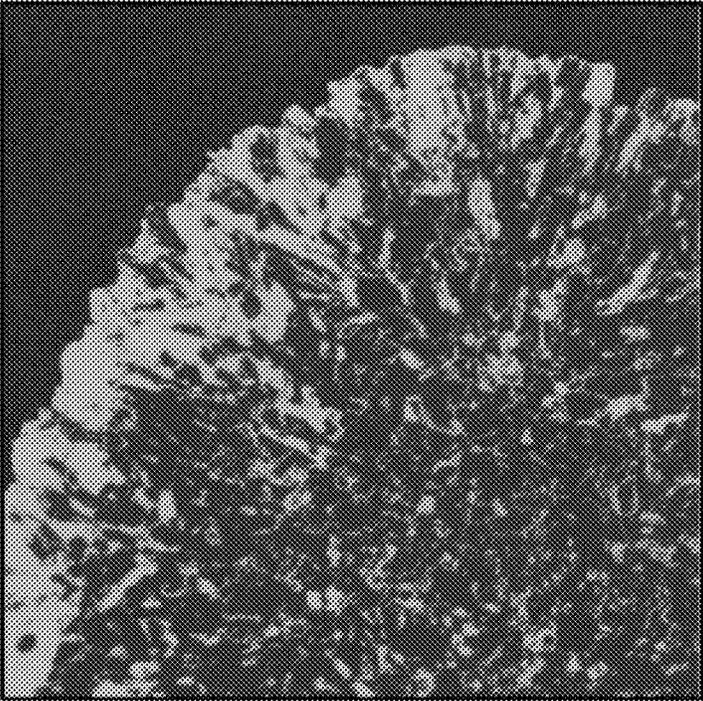
【Fig. 5(b)】



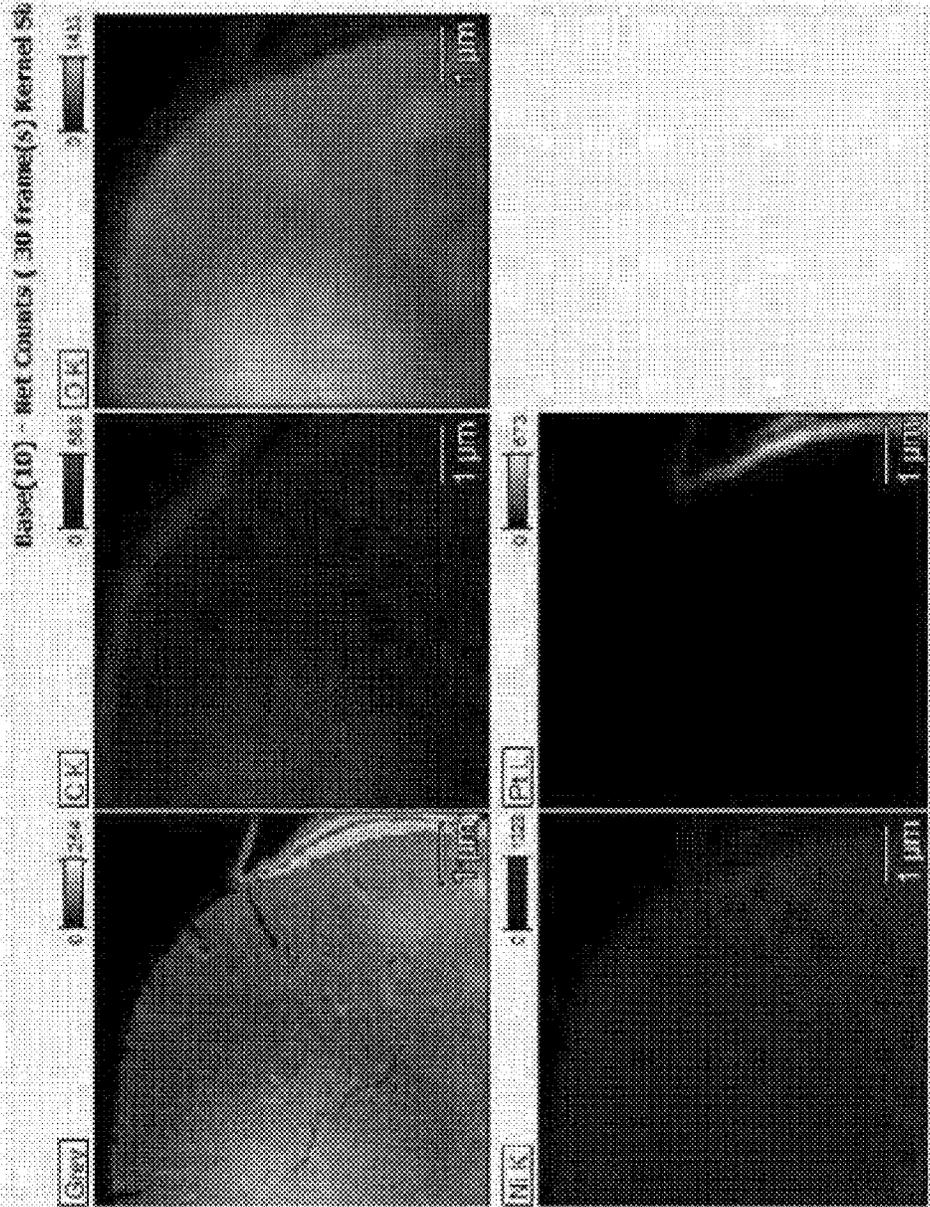
【Fig. 6(a)】



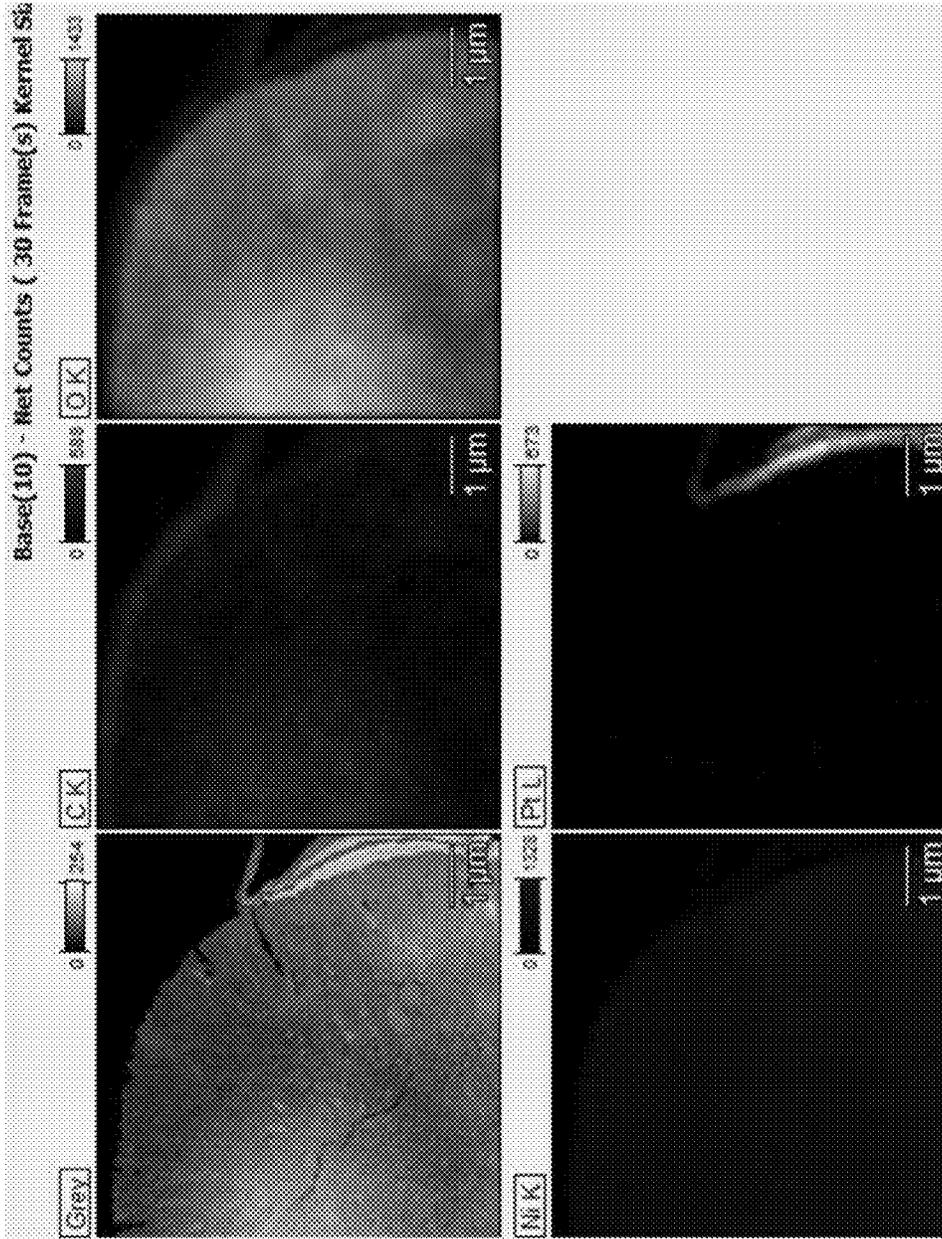
【Fig. 6(b)】



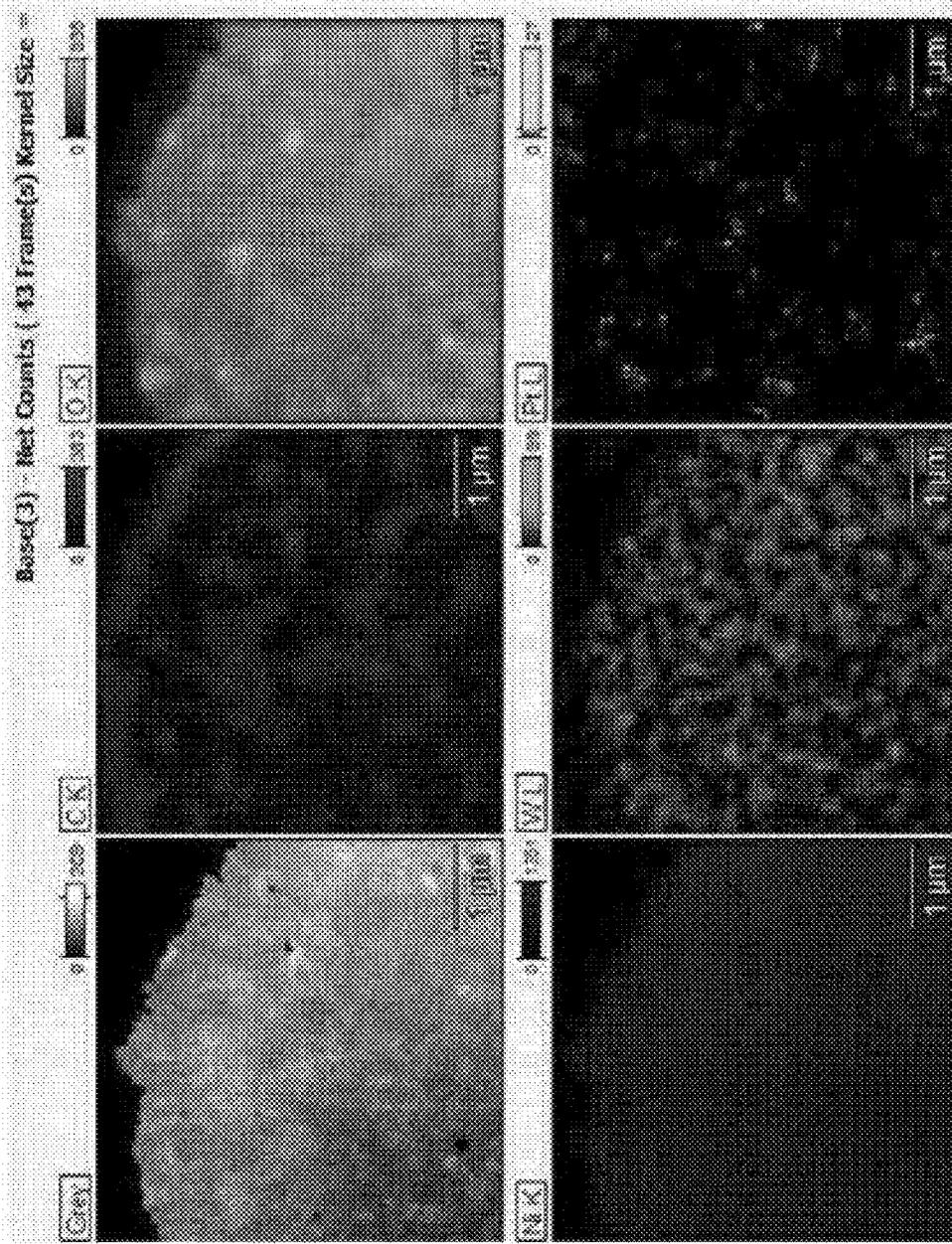
【Fig. 7(a)】



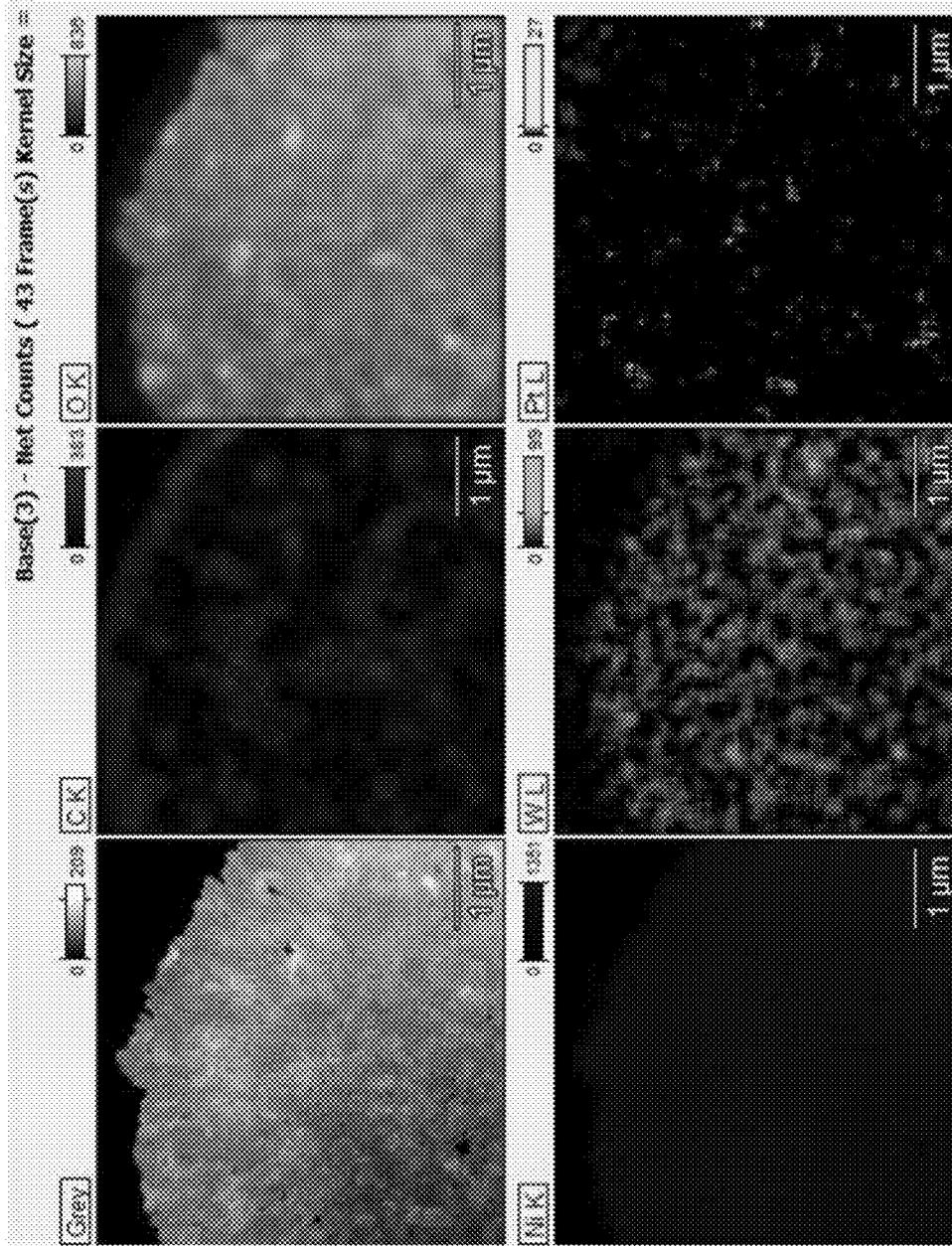
【Fig. 7(b)】



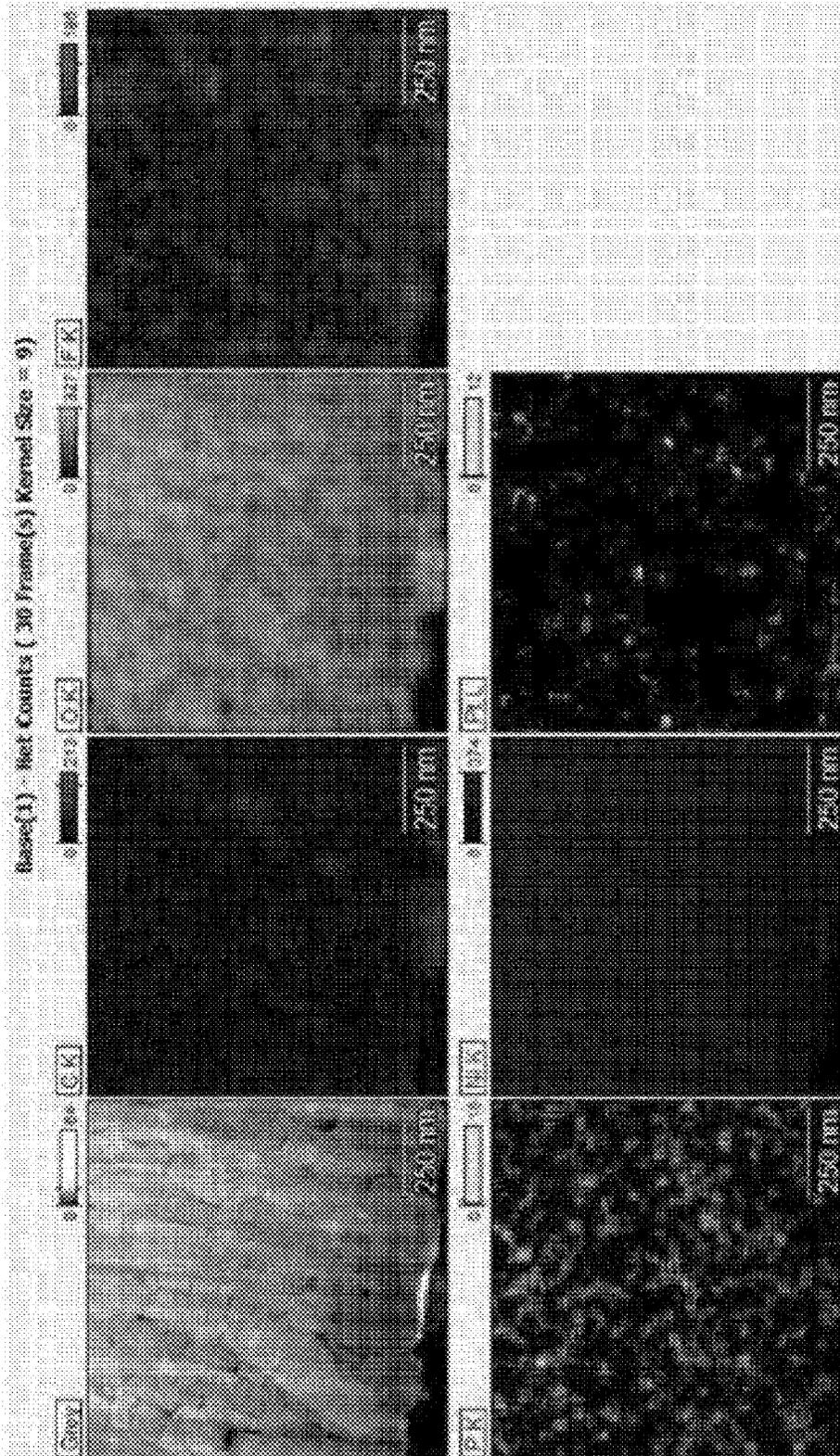
【Fig. 8(a)】



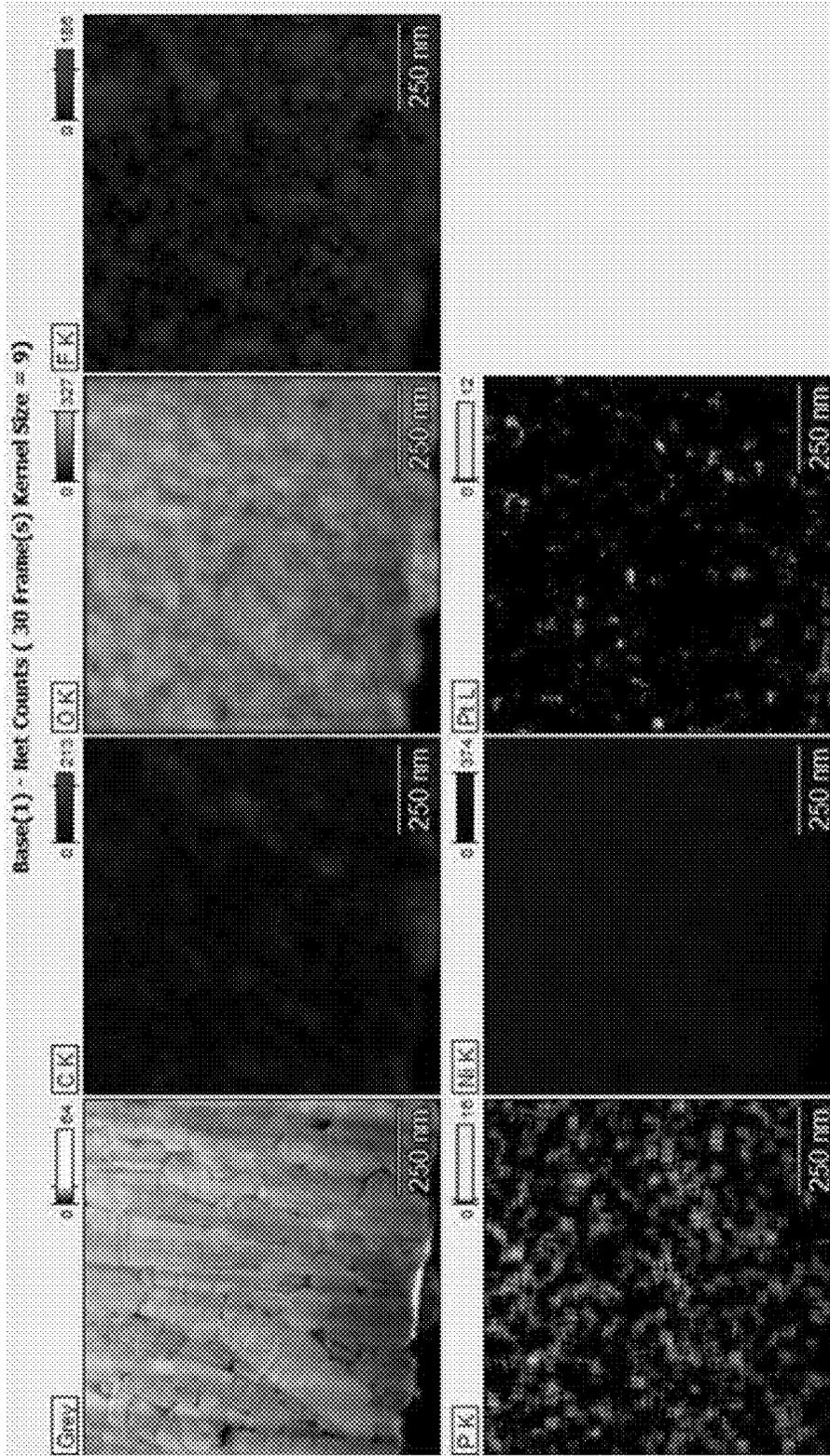
【Fig. 8(b)】



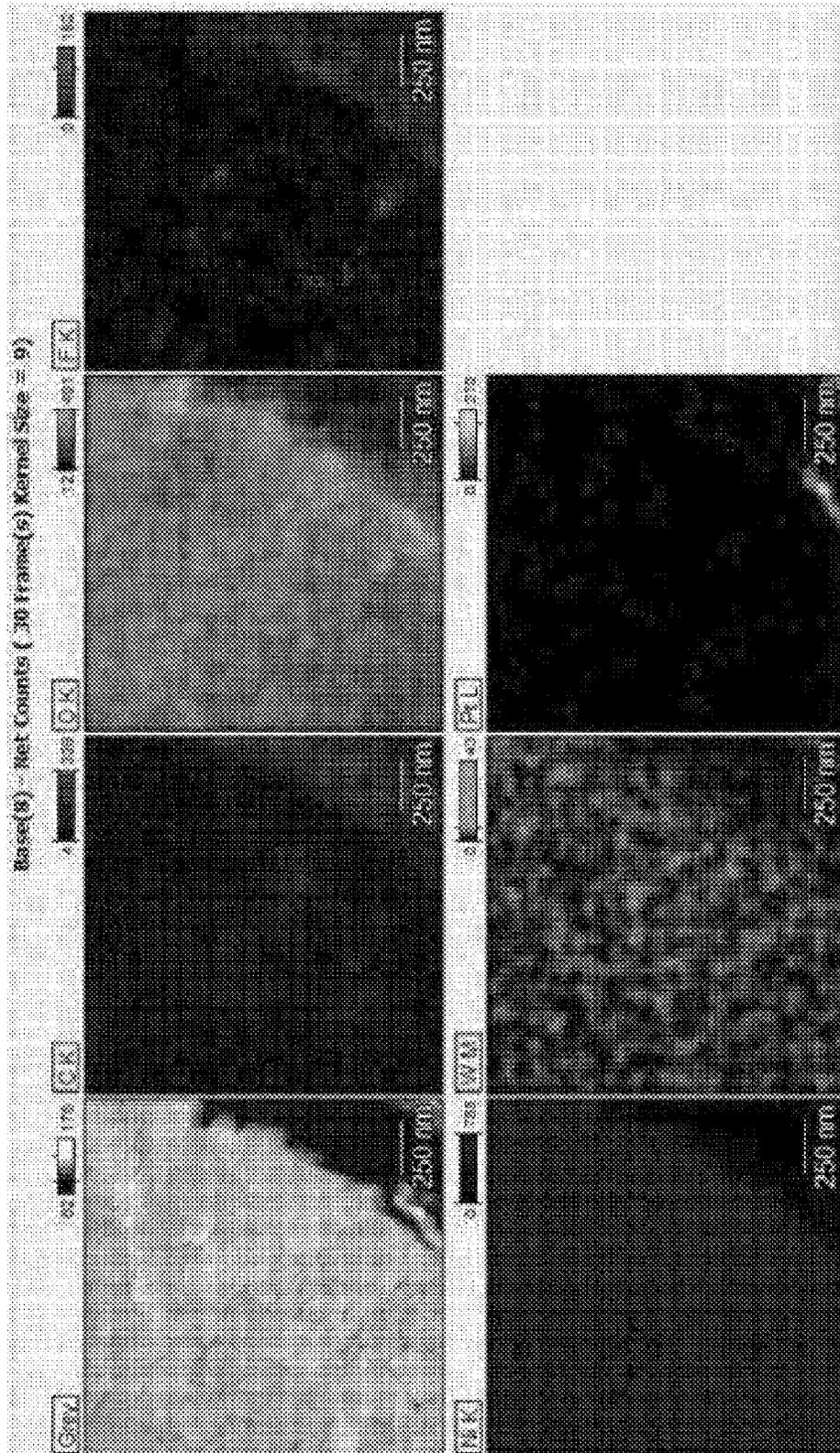
【Fig. 9(a)】



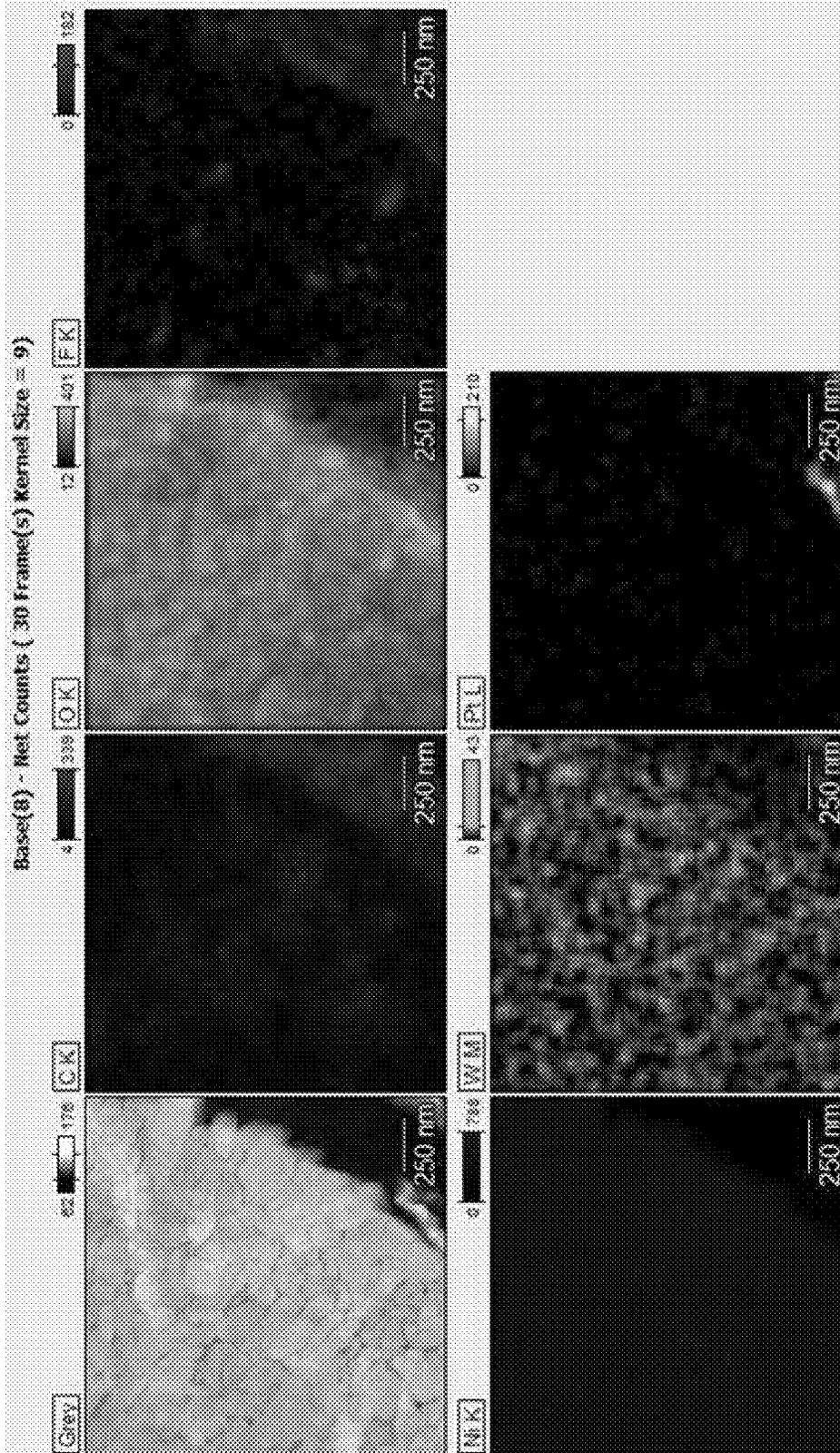
【Fig. 9(b)】



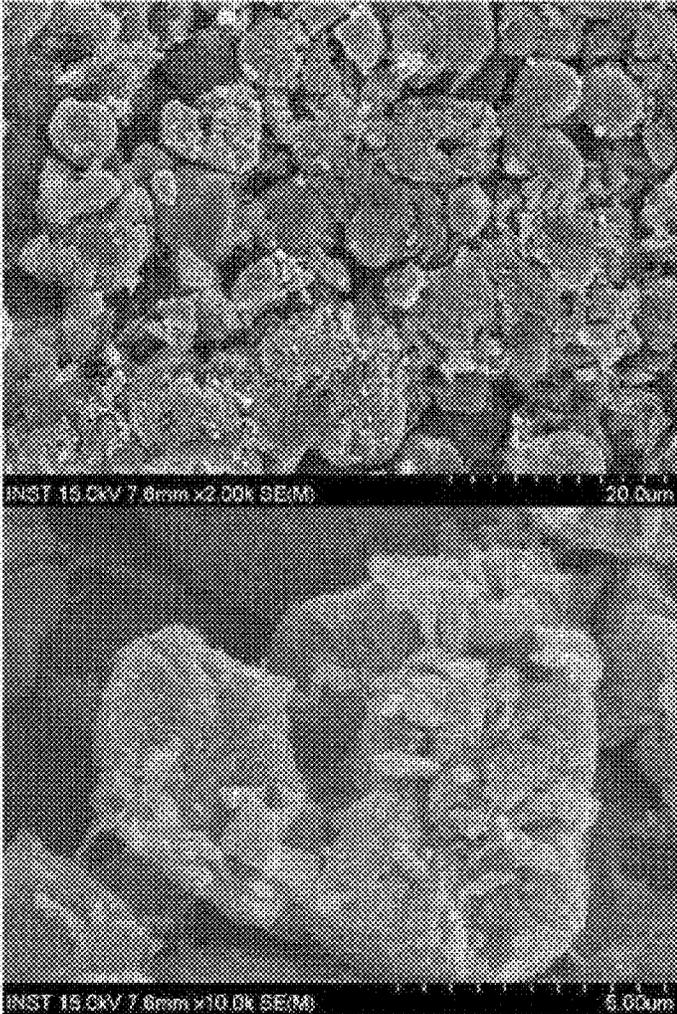
【Fig. 10(a)】



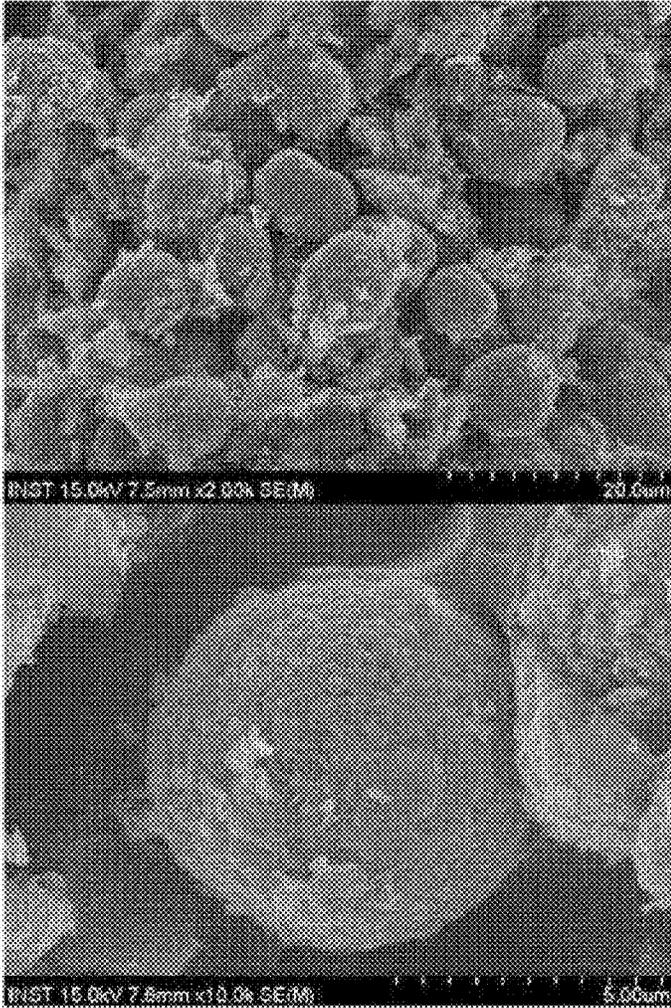
【Fig. 10(b)】



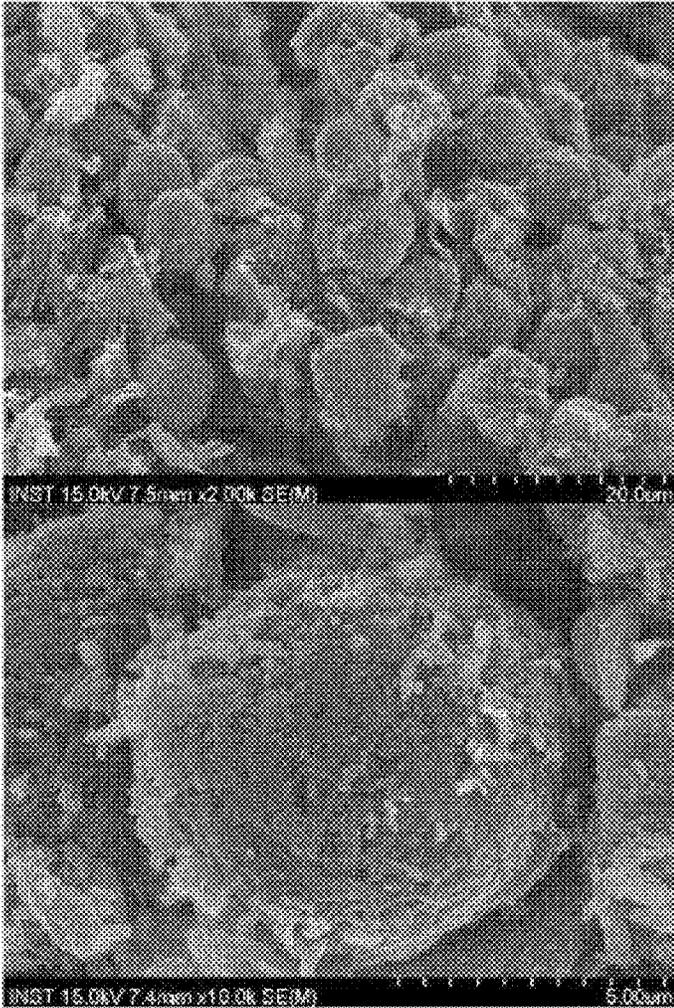
【Fig. 11】



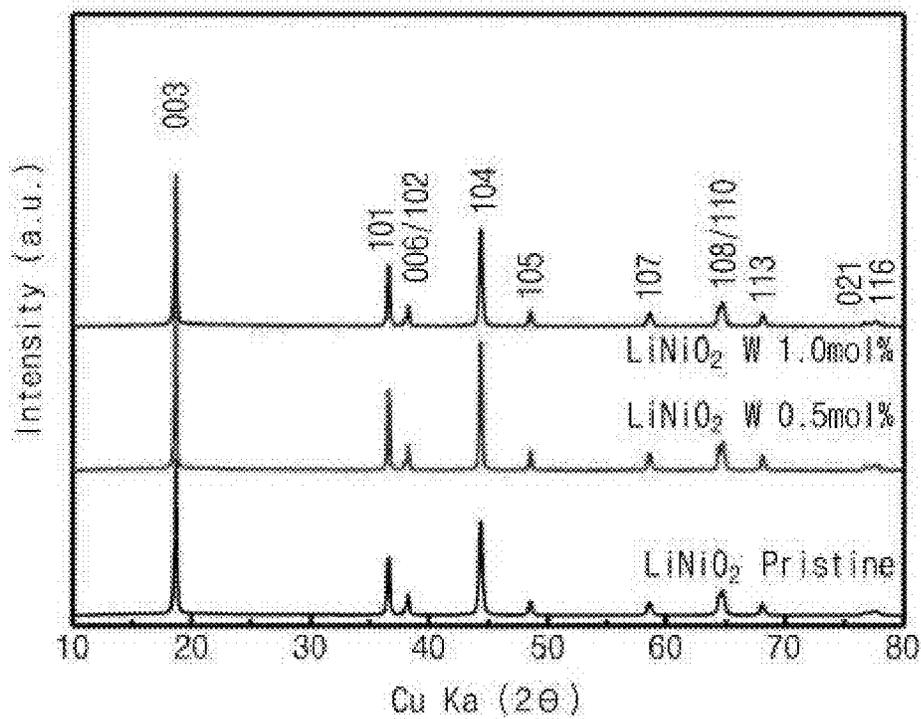
【Fig. 12】

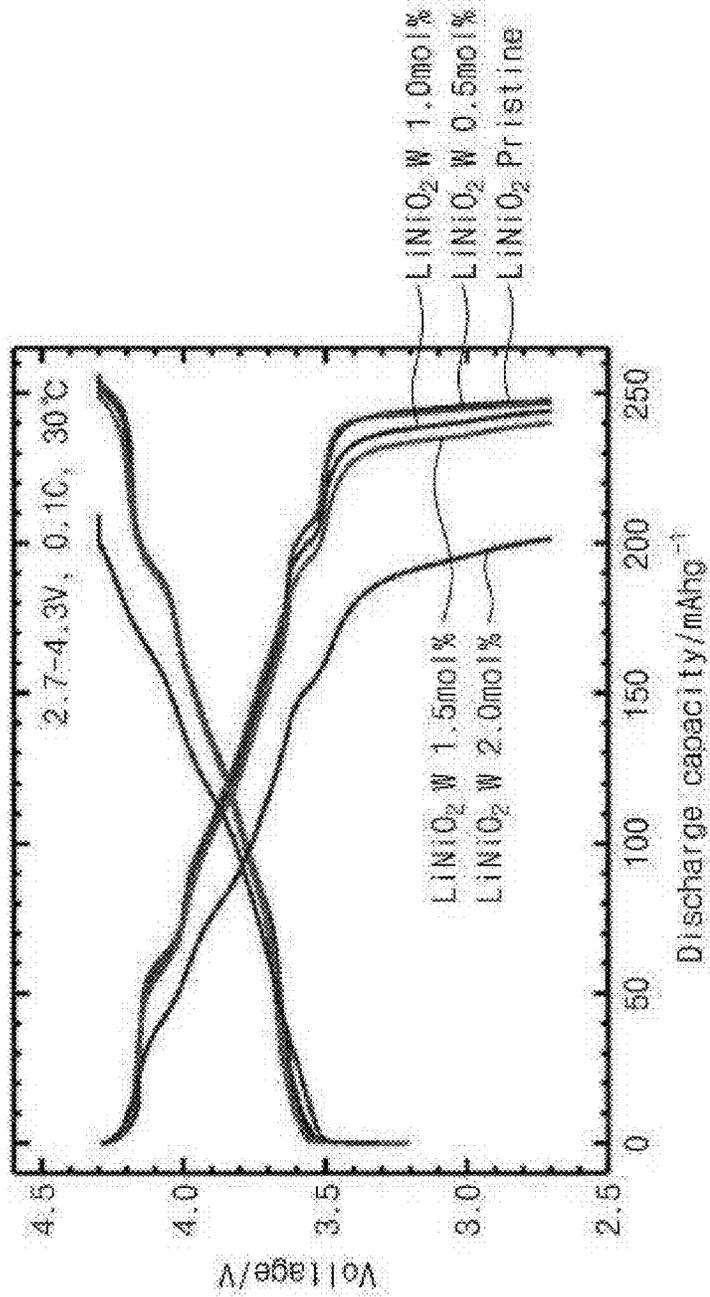


[Fig. 13]

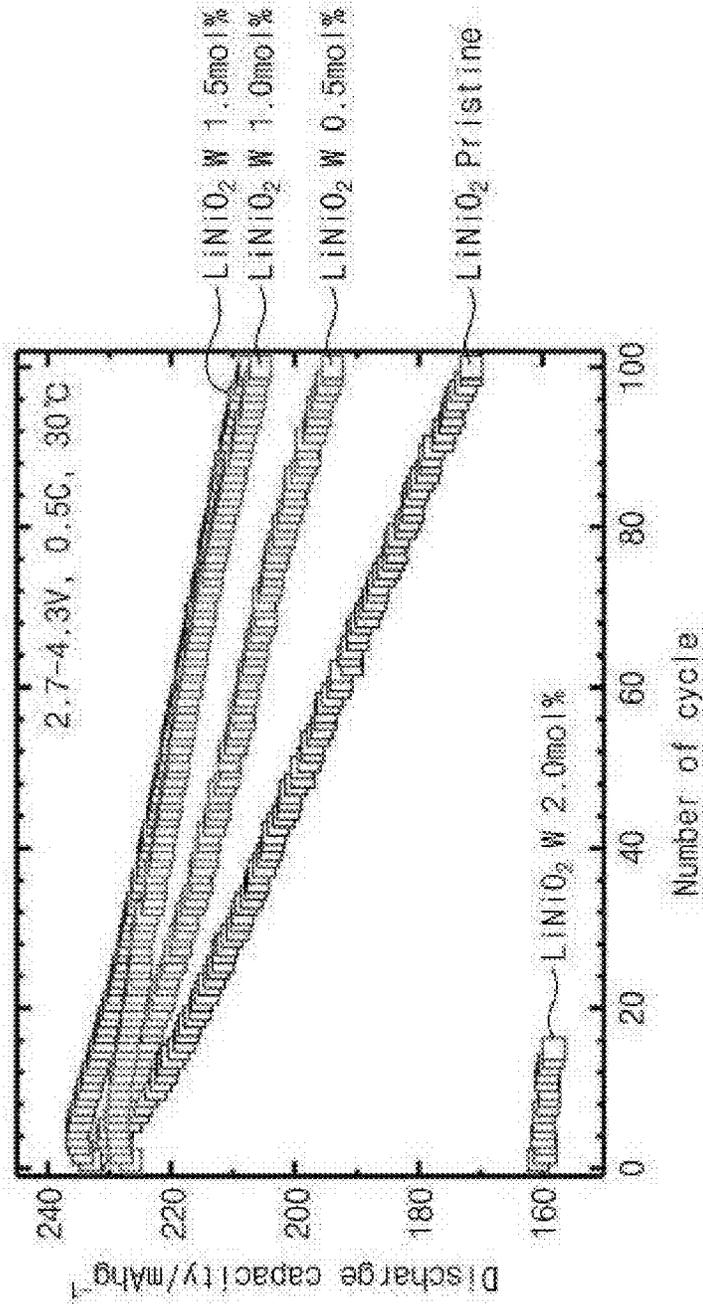


【Fig. 14】



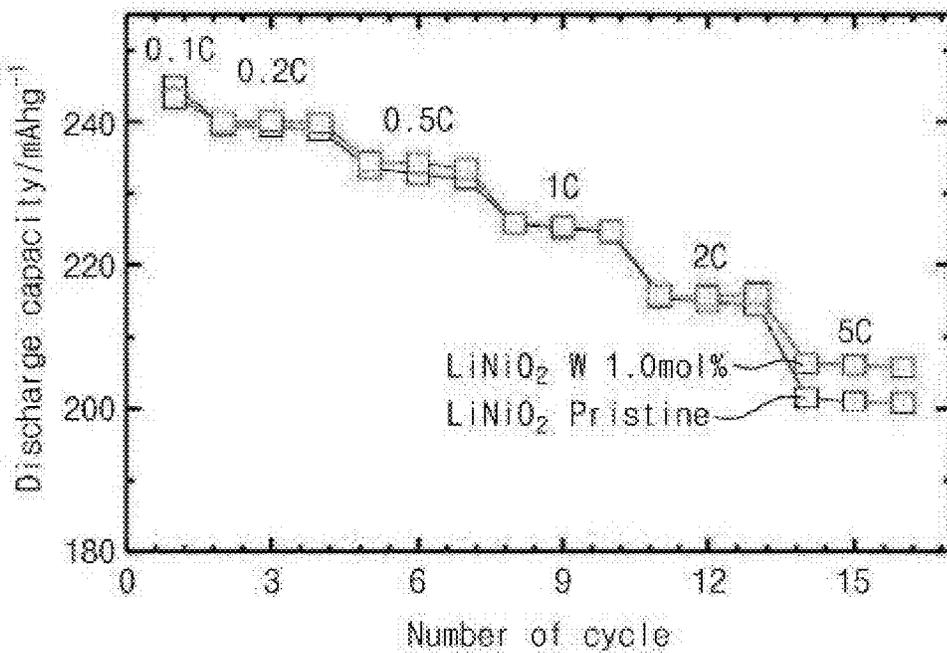


[Fig. 15]

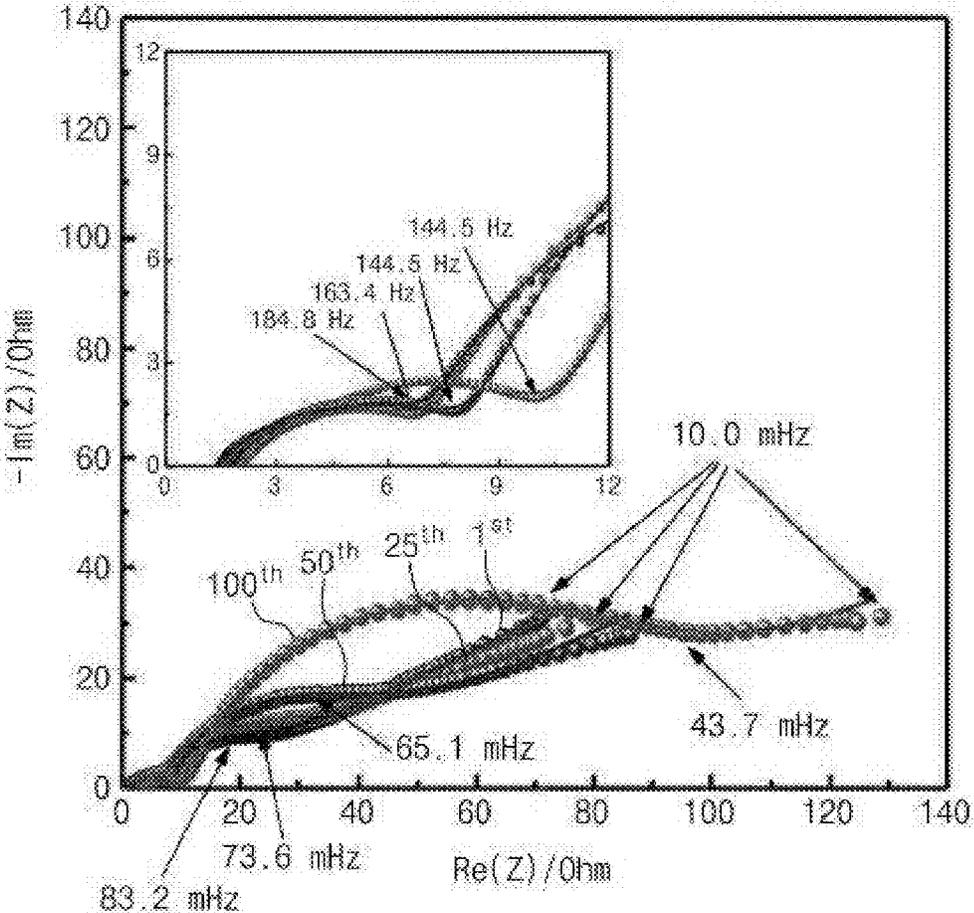


[Fig. 16]

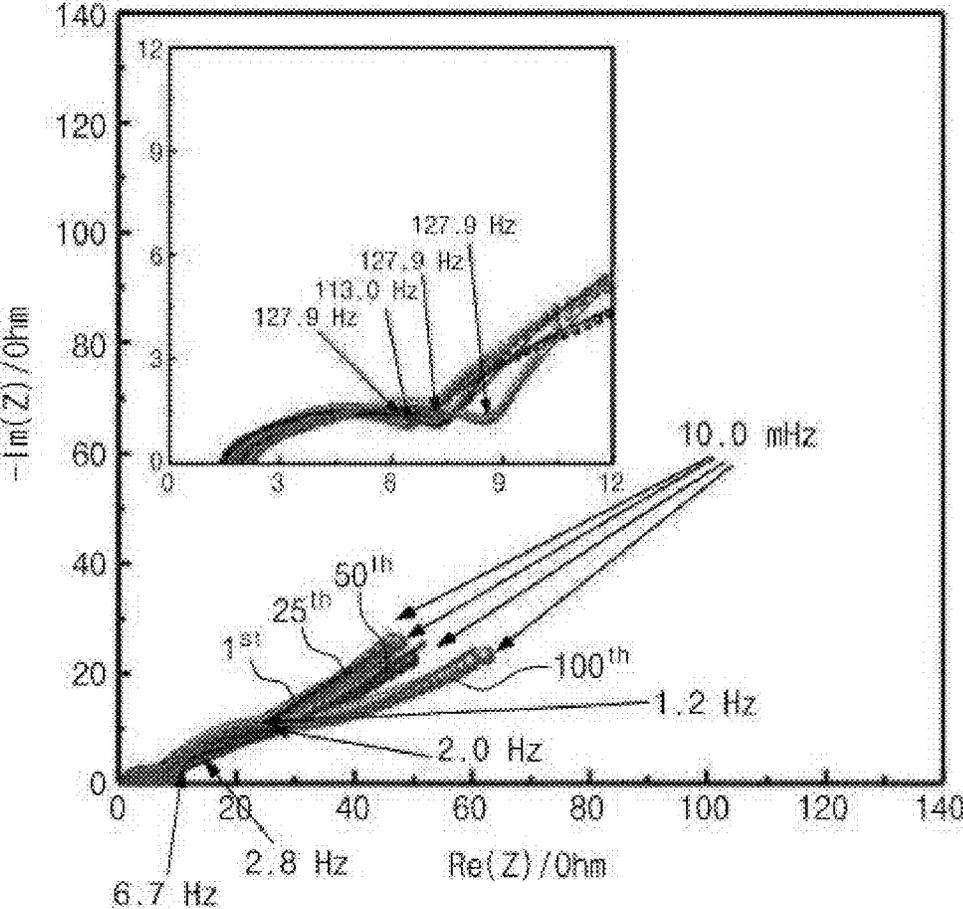
【Fig. 17】



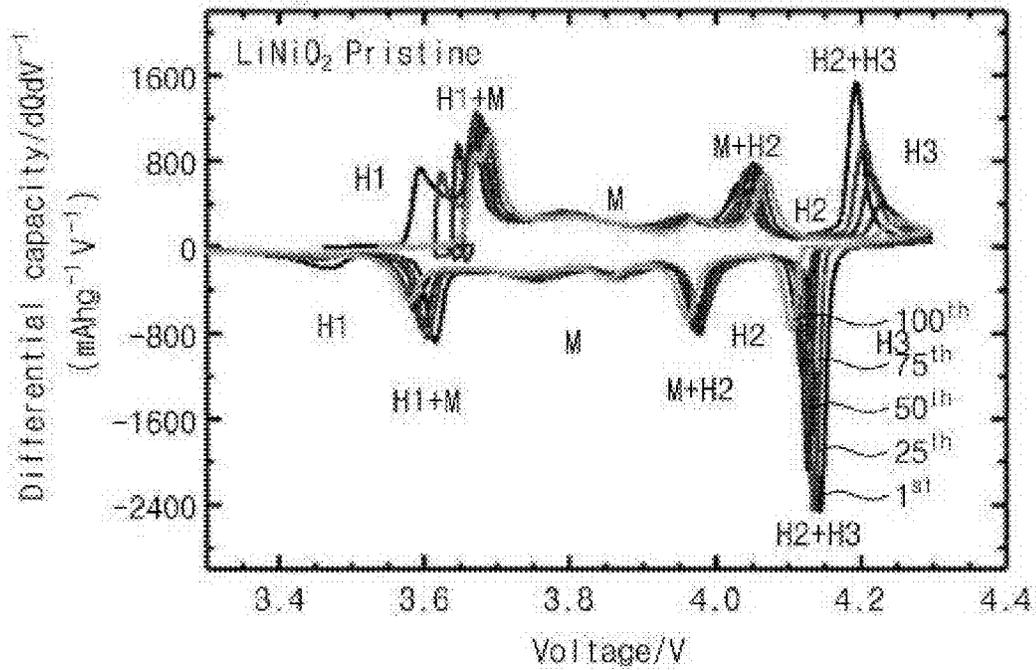
[Fig. 18]



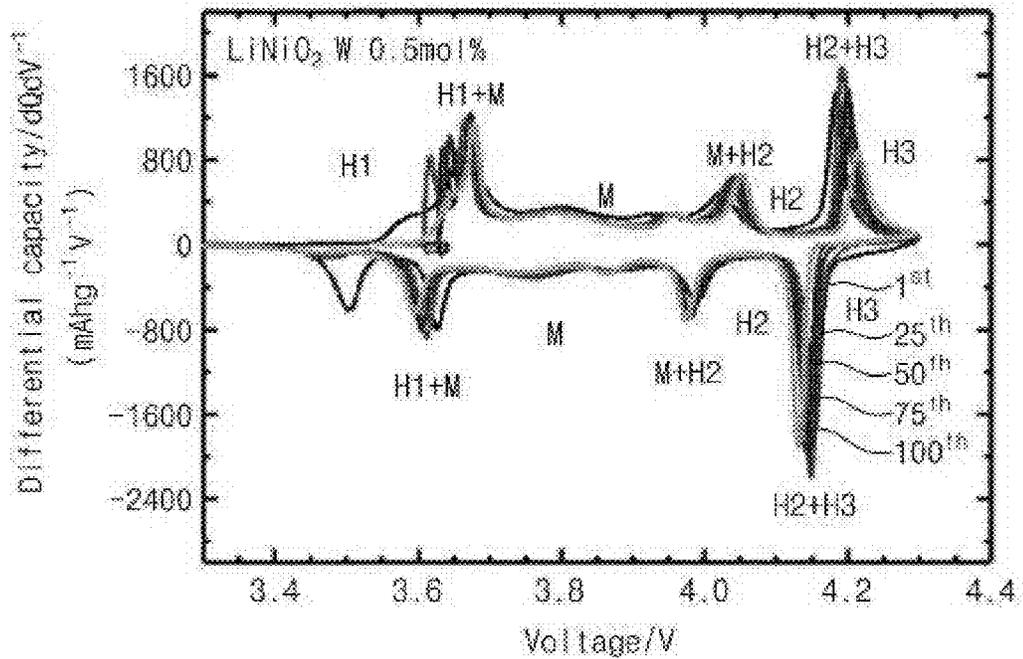
[Fig. 19]



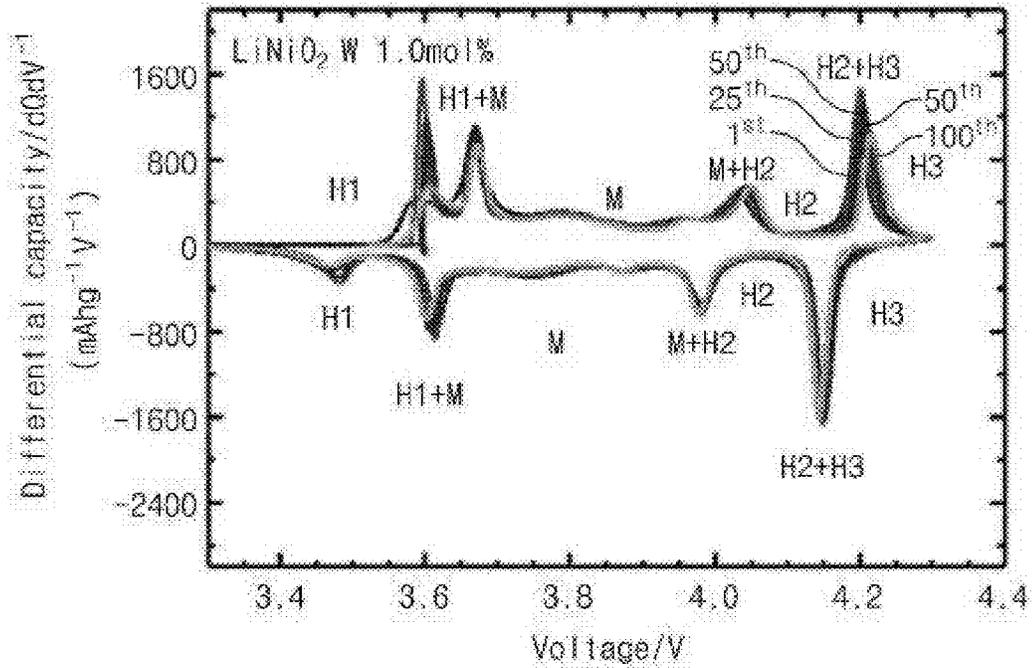
[Fig. 20]



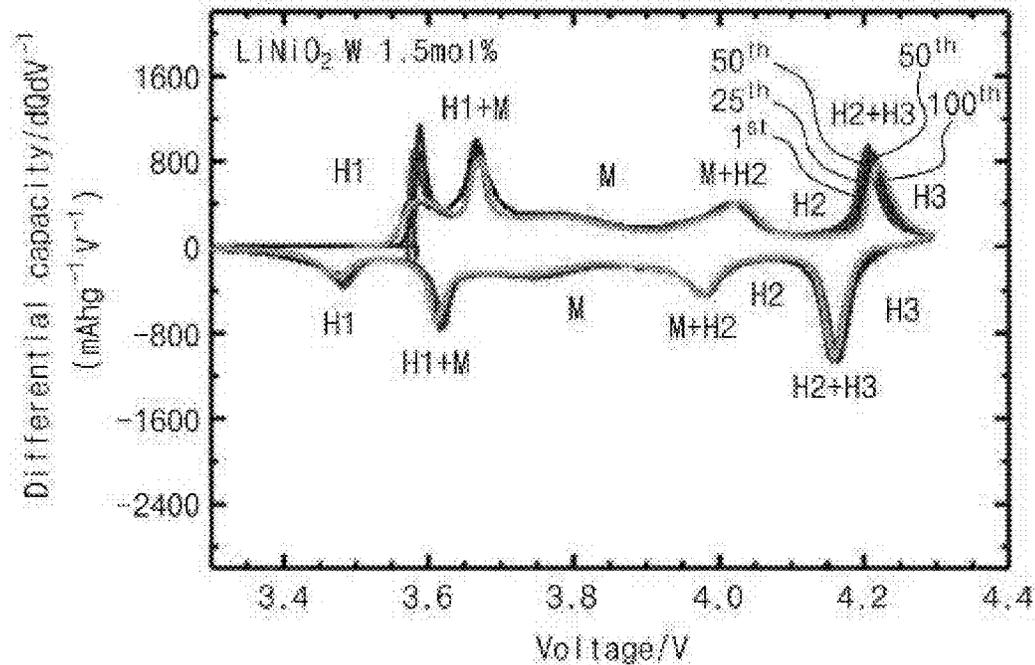
[Fig. 21]



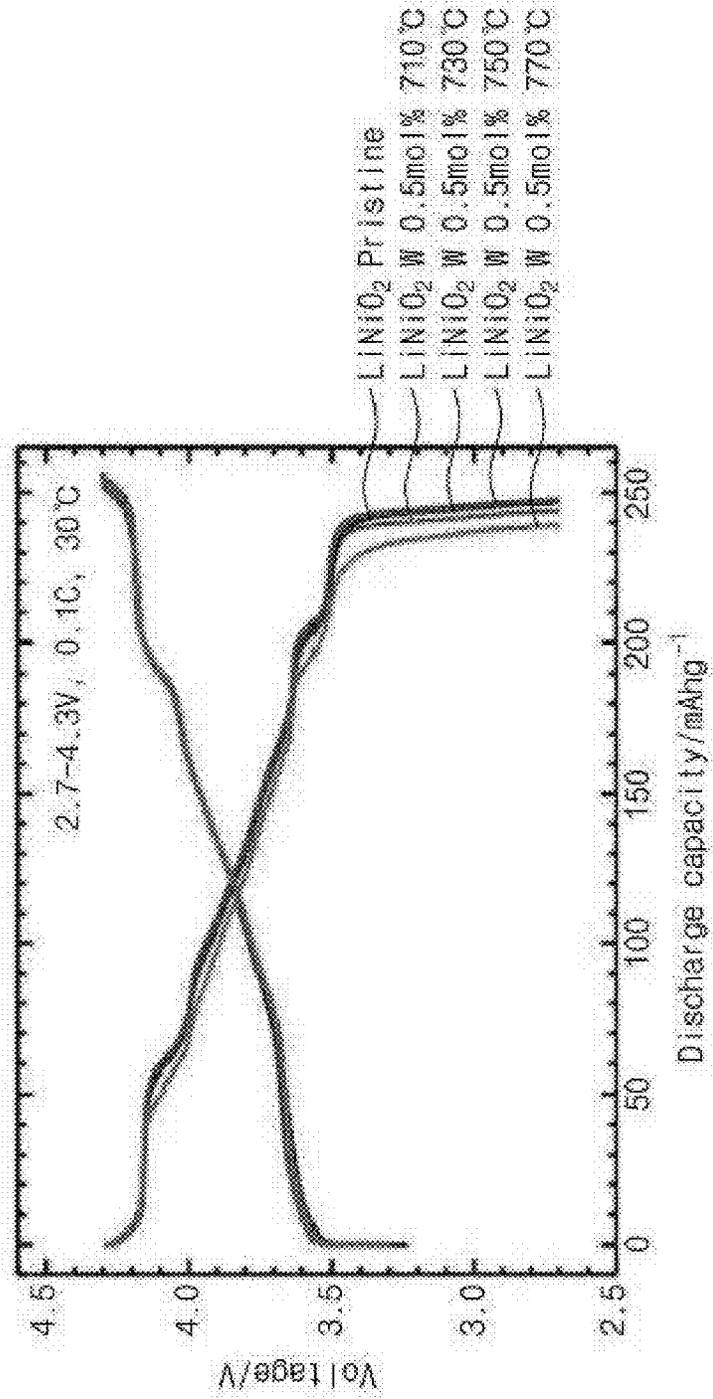
[Fig. 22]

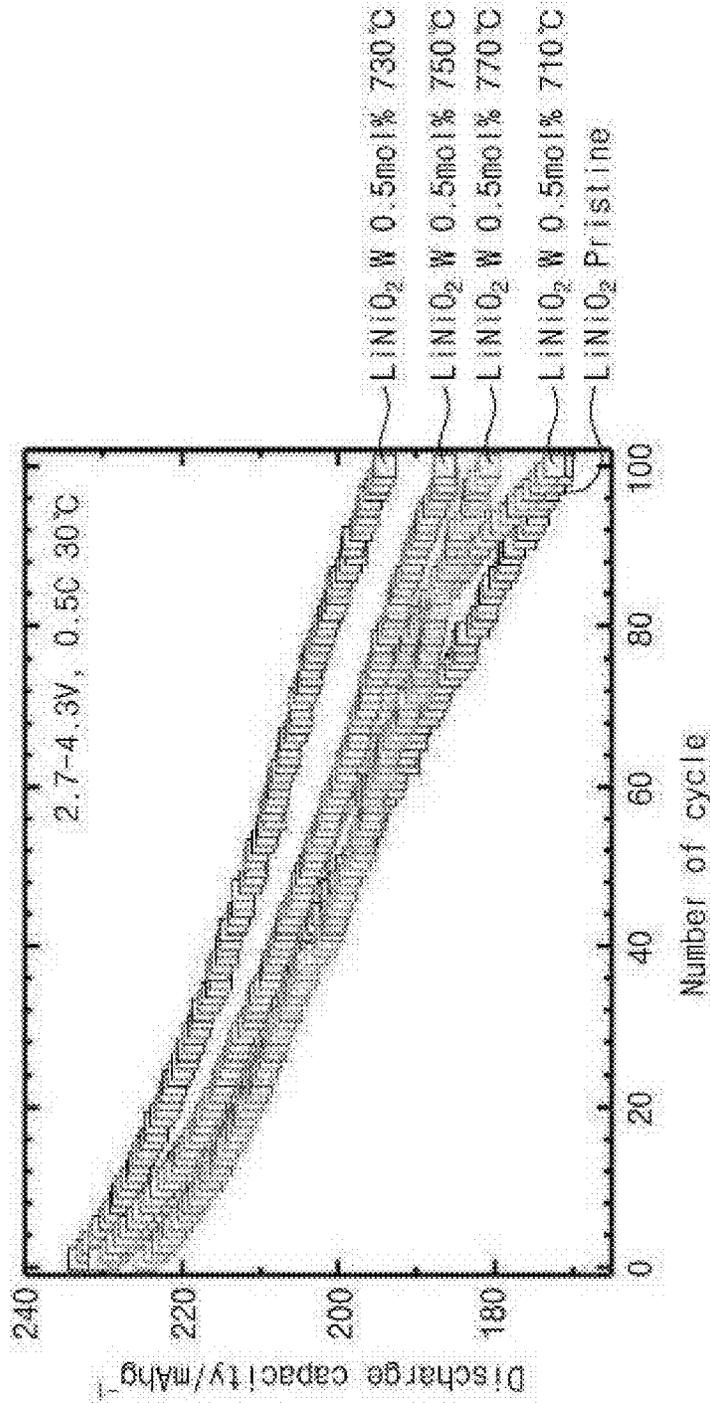


[Fig. 23]

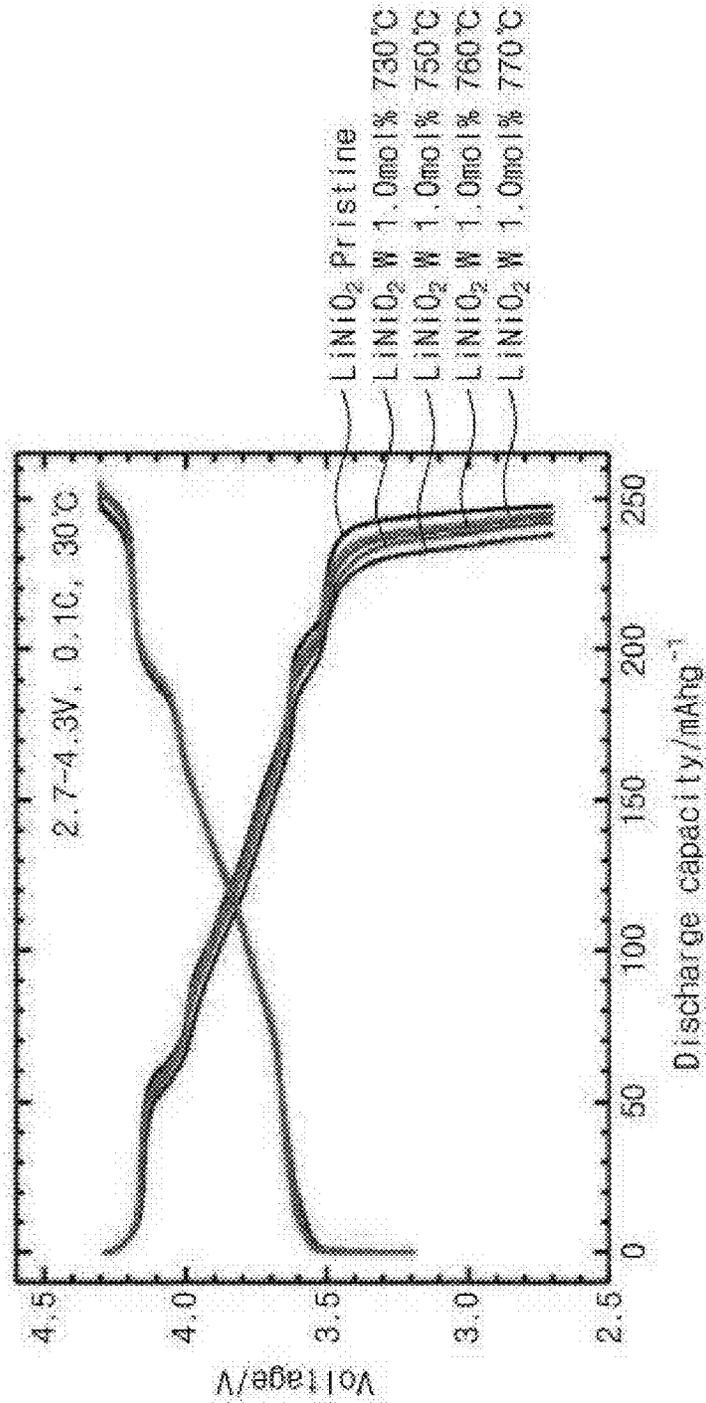


【Fig. 24】

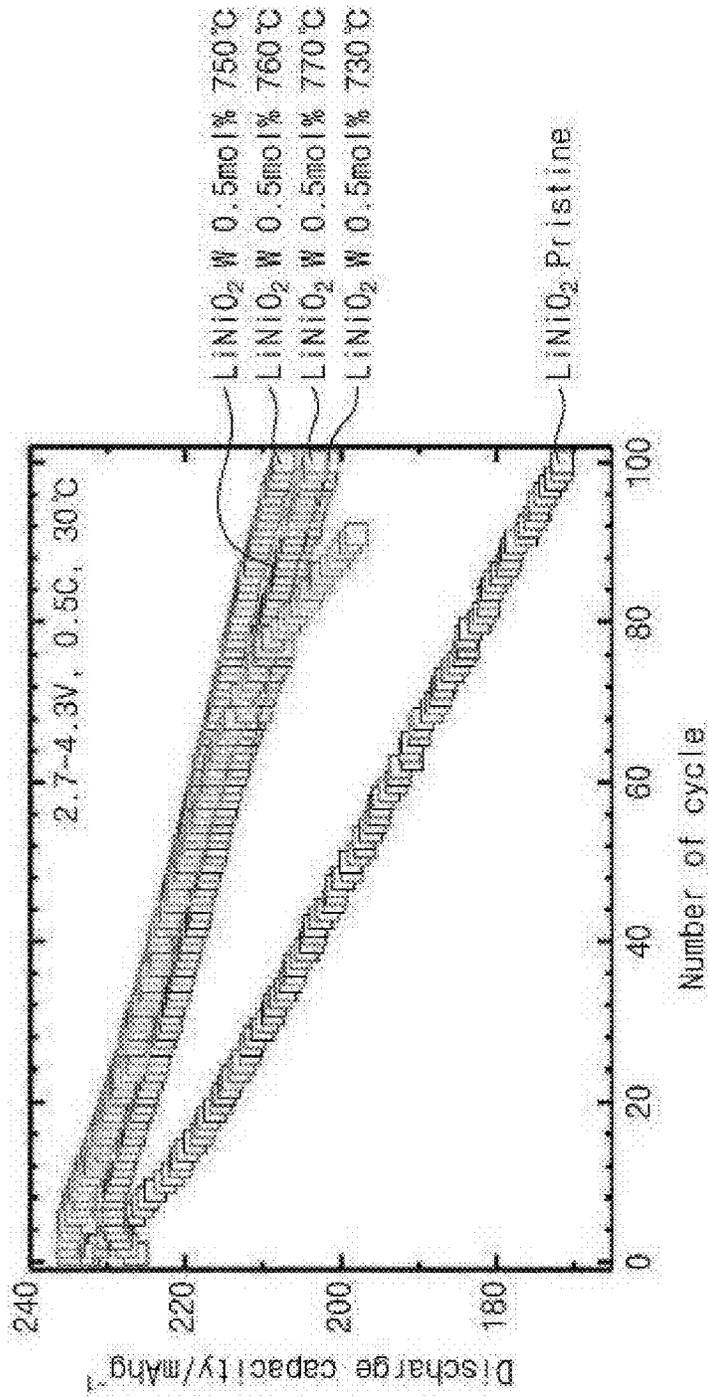




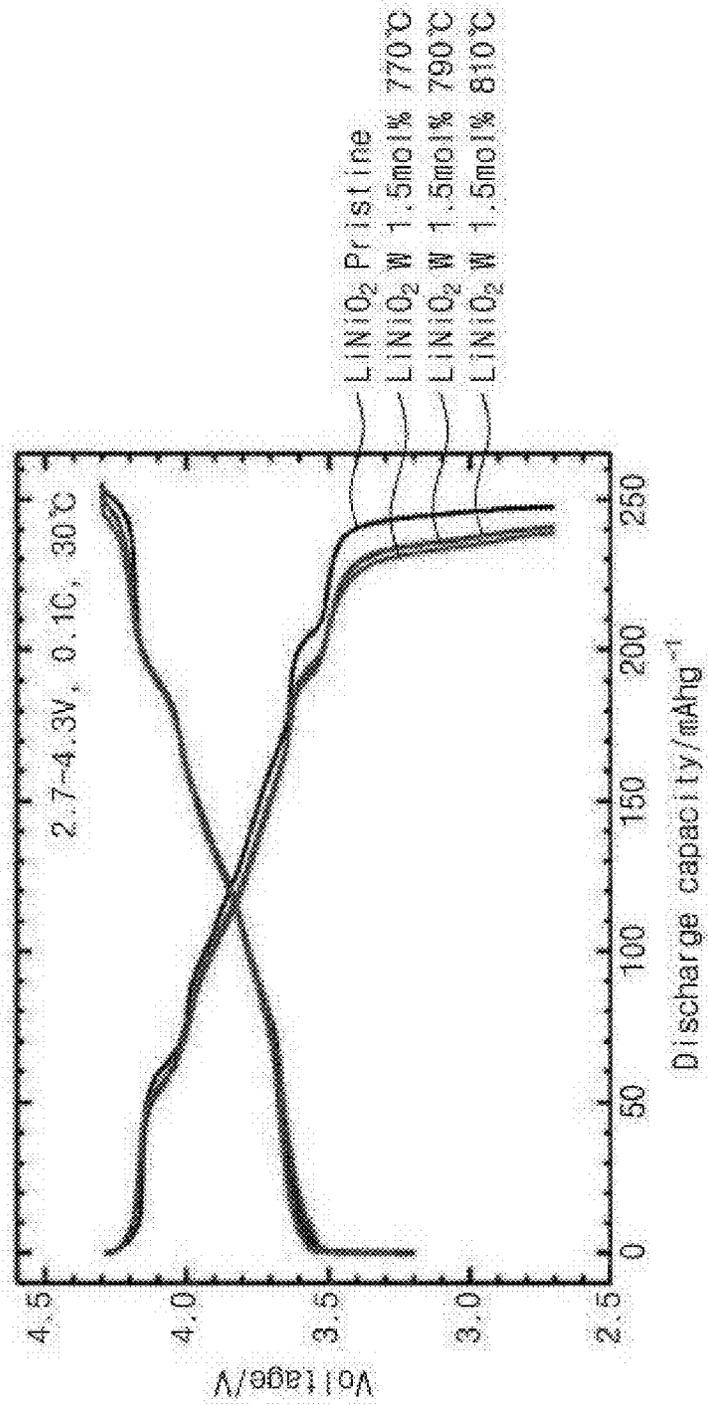
【Fig. 25】



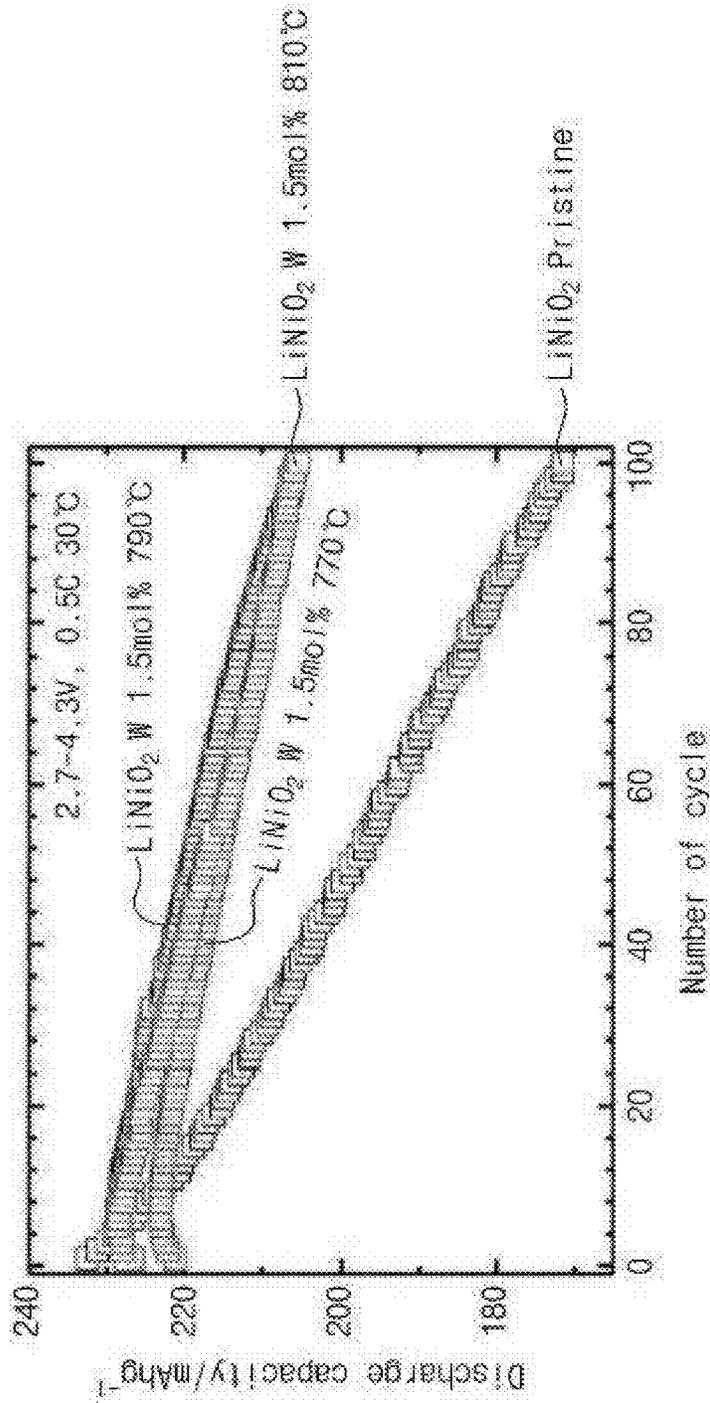
【Fig. 26】



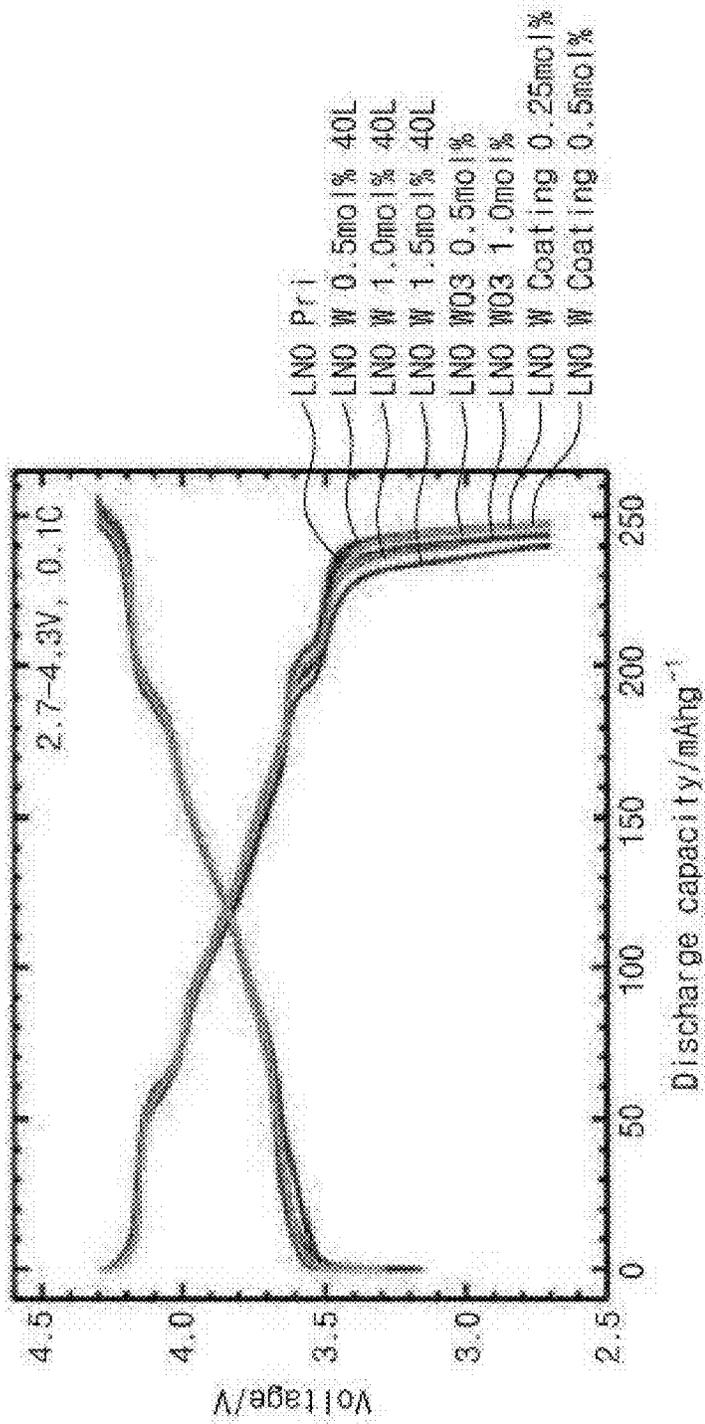
[Fig. 27]



【Fig. 28】

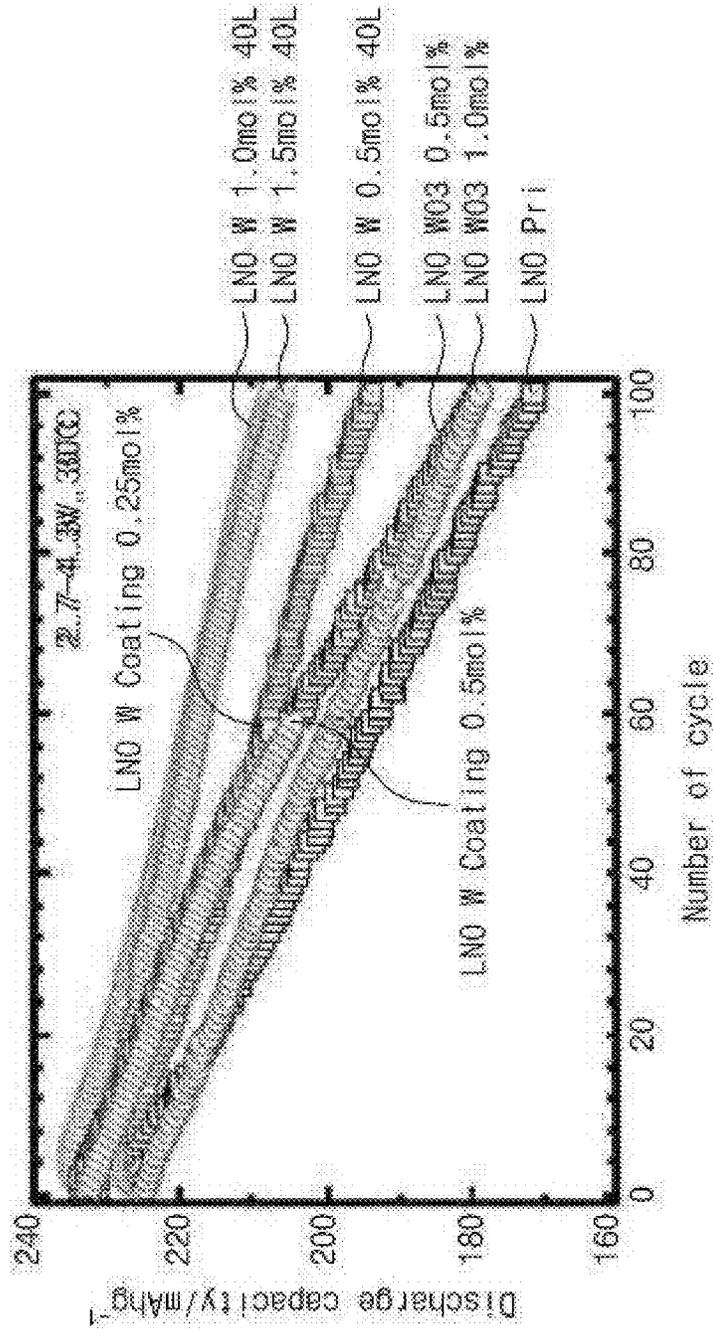


[Fig. 29]

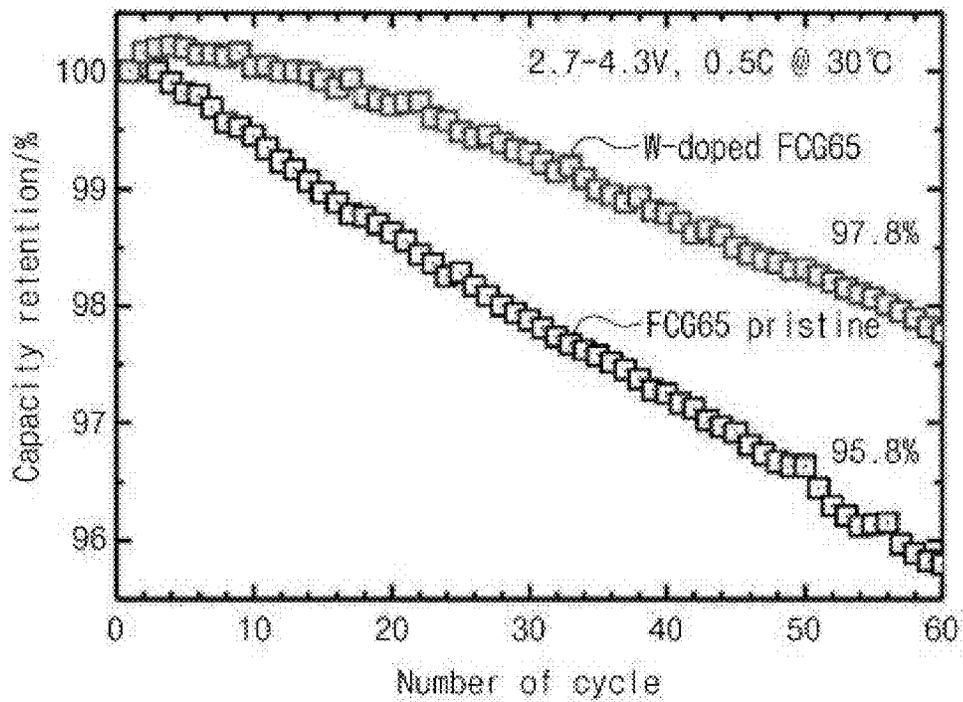


【Fig. 30】

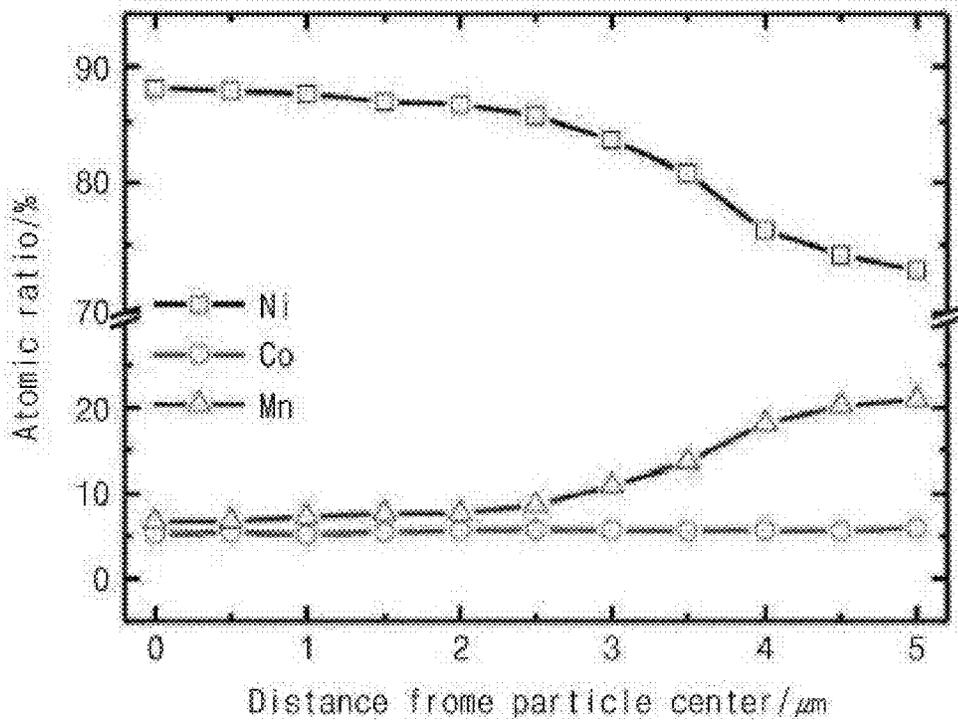
[Fig. 31]



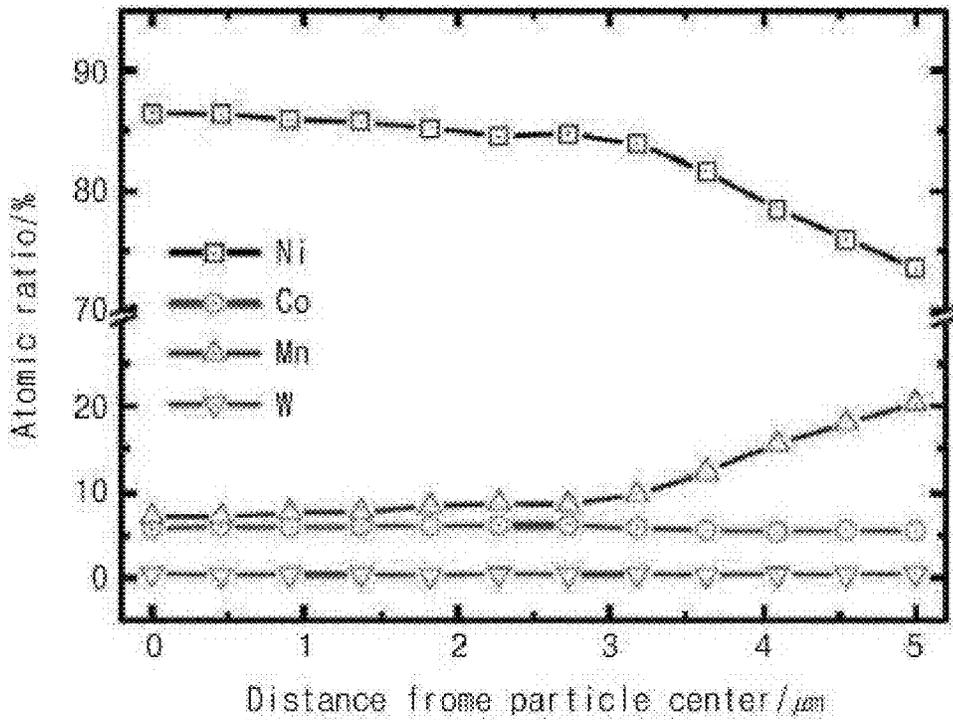
【Fig. 32】



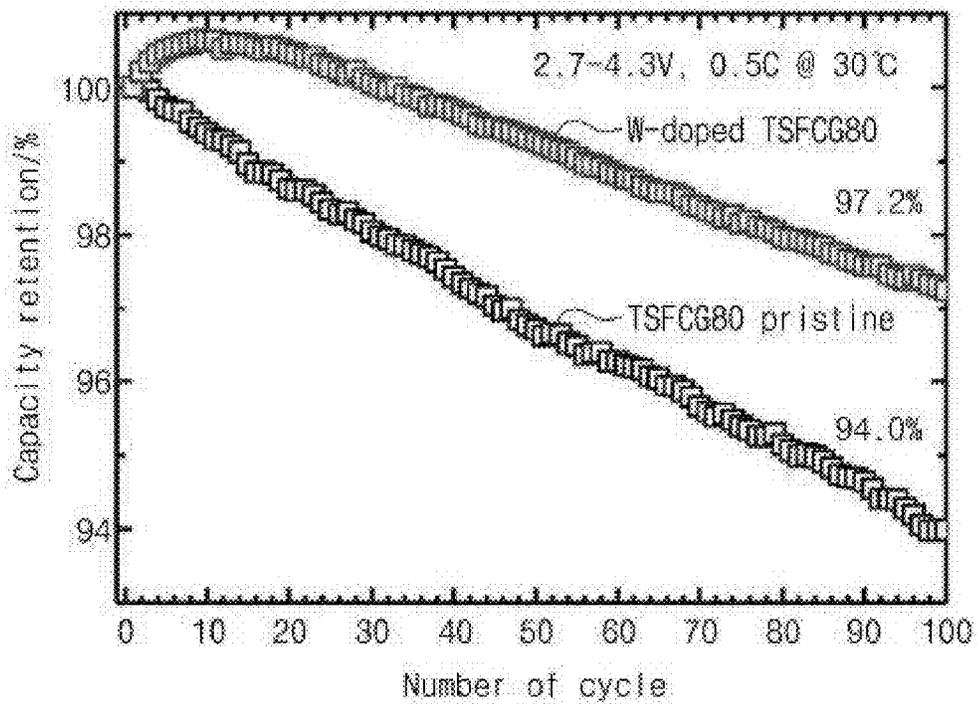
【Fig. 33】



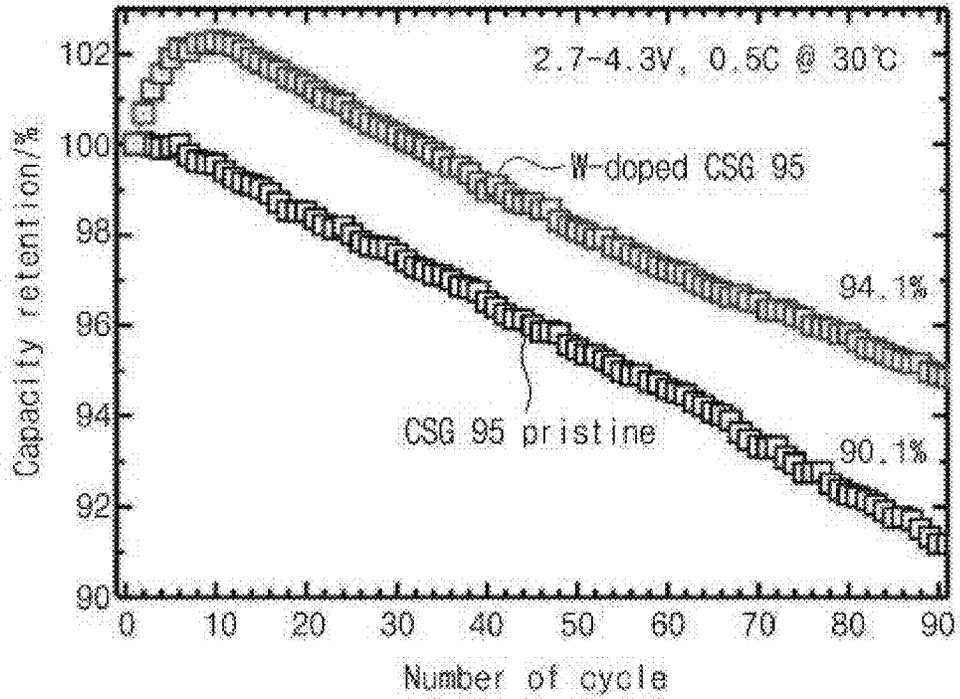
[Fig. 34]



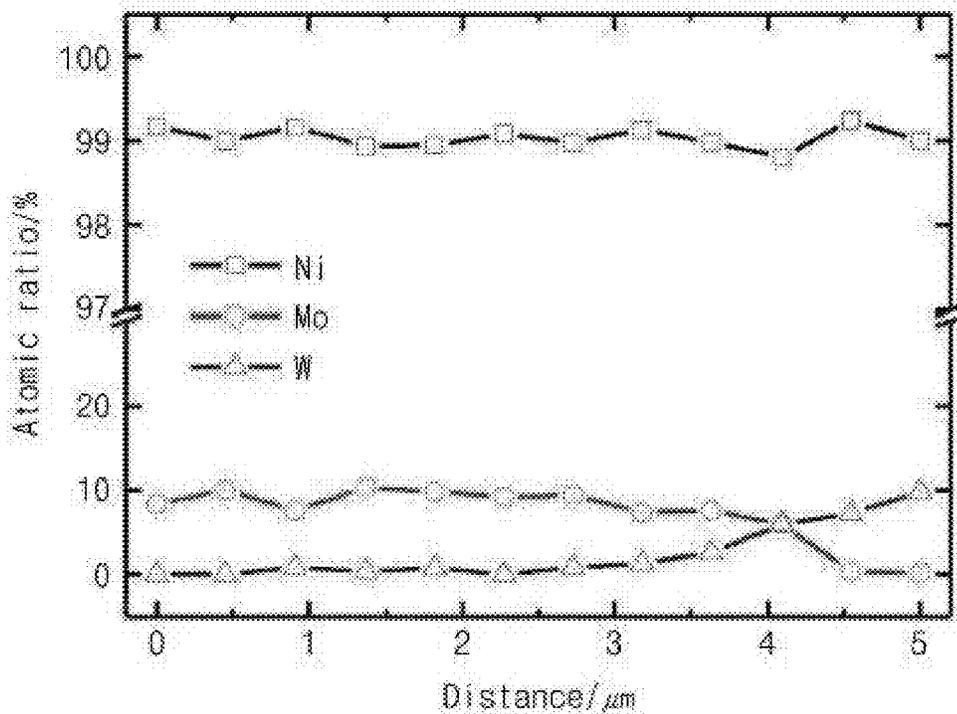
[Fig. 35]



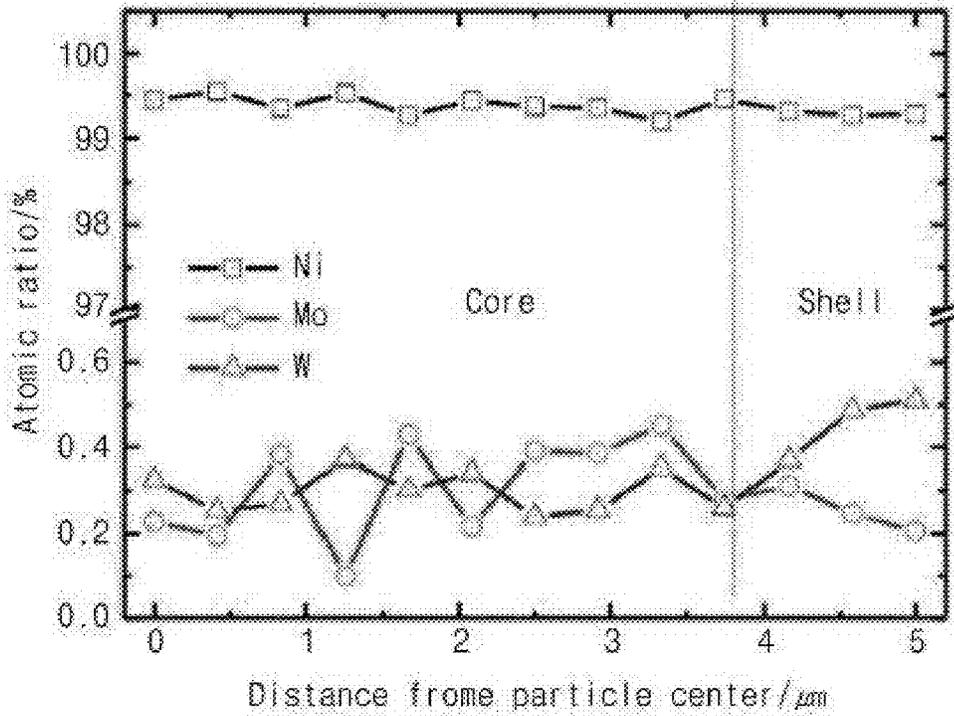
【Fig. 36】



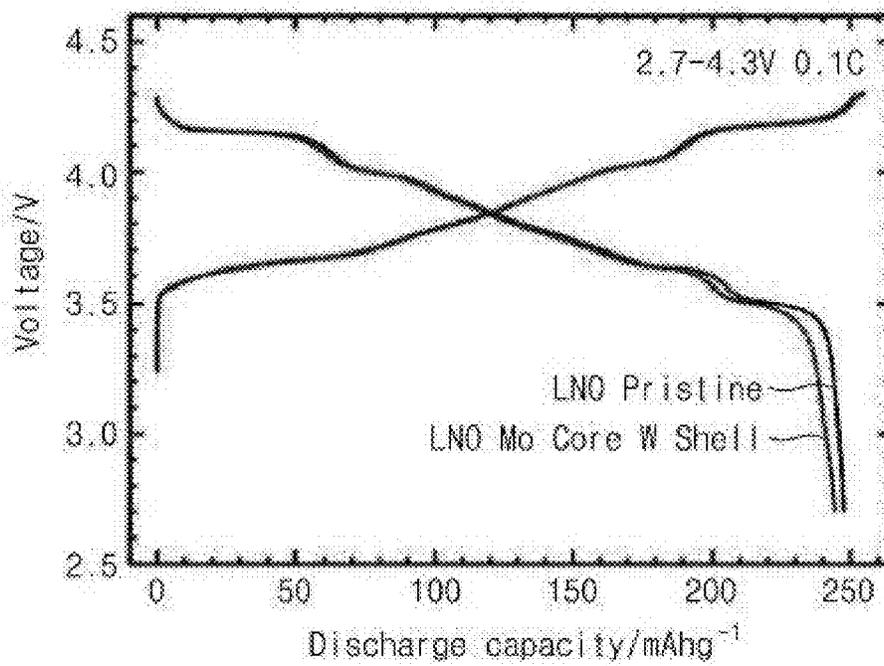
【Fig. 37】



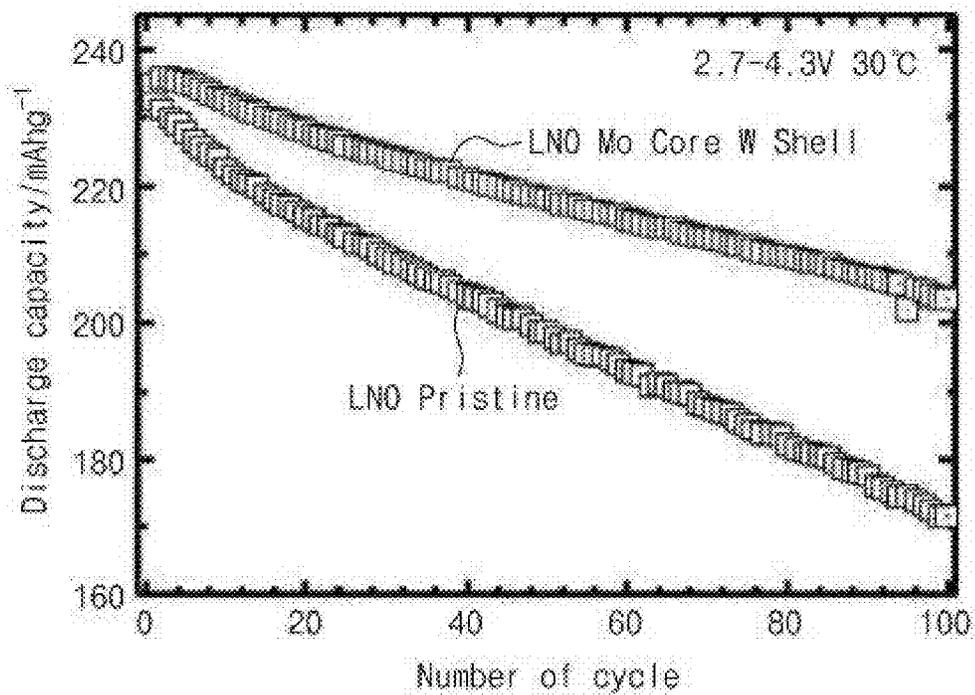
【Fig. 38】



【Fig. 39】



【Fig. 40】



1

**POSITIVE ELECTRODE ACTIVE
MATERIAL, METHOD FOR
MANUFACTURING SAME, AND LITHIUM
SECONDARY BATTERY CONTAINING
SAME**

CROSS-REFERENCE TO RELATED
APPLICATION

This application is a continuation of pending International Application No. PCT/KR2017/002698, which was filed on Mar. 13, 2017 and claims priority to Korean Patent Application Nos. 10-2016-0043718 and 10-2017-0021894, filed on Apr. 8, 2016 and Feb. 17, 2017, in the Korean Intellectual Property Office, the disclosures of which are hereby incorporated by reference in their entireties.

BACKGROUND

1. Field

The present disclosure herein relates to a positive active material, a method of fabricating the same, and a lithium secondary battery including the same.

2. Description of the Related Art

Secondary batteries capable of storing electrical energy have been increasingly demanded with the development of portable mobile electronic devices such as smart phones, MP3 players, and tablet personal computers. In particular, lithium secondary batteries have been increasingly demanded with the development of electric cars, medium and large energy storage systems, and portable devices requiring a high energy density.

Positive active materials used in the lithium secondary batteries have been studied due to the increase in demand for the lithium secondary batteries. For example, Korean Patent Publication No. 10-2014-0119621 (Application No. 10-2013-0150315) discloses a secondary battery manufactured using a precursor for fabricating a lithium-rich positive active material, which is represented by $Ni_{\alpha}Mn_{\beta}Co_{\gamma}\delta A\delta CO_3$, where 'A' is one or two or more selected from a group consisting of B, Al, Ga, Ti, and In, ' α ' ranges from 0.05 to 0.4, ' β ' ranges from 0.5 to 0.8, ' γ ' ranges from 0 to 0.4, and ' δ ' ranges from 0.001 to 0.1. In this Korean Patent Publication, the secondary battery may have a high-voltage capacity and long life characteristics by adjusting a kind and a composition of a metal substituted in the precursor and by adjusting a kind and the amount of an added metal.

SUMMARY

The present disclosure may provide a highly reliable positive active material, a method of fabricating the same, and a lithium secondary battery including the same.

The present disclosure may also provide a high-capacity positive active material, a method of fabricating the same, and a lithium secondary battery including the same.

The present disclosure may further provide a long-life positive active material, a method of fabricating the same, and a lithium secondary battery including the same.

The present disclosure may further provide a positive active material with improved thermal stability, a method of fabricating the same, and a lithium secondary battery including the same.

2

In an aspect, a positive active material may include lithium, an additive metal, and at least one of nickel, cobalt, manganese, or aluminum. The additive metal may include an element different from nickel, cobalt, manganese, and aluminum, and an average content of the additive metal may be less than 2 mol %. A concentration of at least one of nickel, cobalt, manganese, or aluminum may be changed in a particle.

In an embodiment, at least one of nickel, cobalt, manganese, or aluminum may have a concentration gradient in a whole of the particle.

In an embodiment, the additive metal may have a substantially constant concentration in a whole of the particle.

In an embodiment, the particle may include a core portion and a shell portion surrounding the core portion. At least one of nickel, cobalt, manganese, or aluminum may have a concentration gradient in one of the core portion and the shell portion, and a concentration of at least one of nickel, cobalt, manganese, or aluminum may be substantially constant in the other of the core portion and the shell portion.

In an embodiment, a concentration gradient of at least one of nickel, cobalt, manganese, or aluminum may be changed in the particle.

In an embodiment, the positive active material may include a first crystal structure and a second crystal structure which have different crystal systems from each other. Ratios of the first crystal structure and the second crystal structure may be adjusted depending on the content of the additive metal.

In an embodiment, the first crystal structure may be a cubic crystal structure, and the second crystal structure may be a trigonal or rhombohedral crystal structure. The ratio of the first crystal structure may increase as the content of the additive metal increases.

In an embodiment, the additive metal may include at least one of tungsten, molybdenum, zirconium, niobium, tantalum, titanium, rubidium, bismuth, magnesium, zinc, gallium, vanadium, chromium, calcium, strontium, or tin.

In an aspect, a positive active material may include a first crystal structure and a second crystal structure, which have different crystal systems from each other. The positive active material may include a first portion in which a ratio of the first crystal structure is higher than a ratio of the second crystal structure; and a second portion in which a ratio of the second crystal structure is higher than a ratio of the first crystal structure. The positive active material may include lithium, an additive metal, and at least one of nickel, cobalt, manganese, or aluminum. The additive metal may include an element different from nickel, cobalt, manganese, and aluminum, and a concentration of at least one of nickel, cobalt, manganese, or aluminum may be changed in a particle.

In an embodiment, the first portion may surround at least a portion of the second portion.

In an embodiment, the positive active material may include primary particles, and a secondary particle in which the primary particles are aggregated. At least one of the primary particles may include both the first crystal structure and the second crystal structure.

In an embodiment, the primary particle including both the first crystal structure and the second crystal structure may be provided at a boundary of the first portion and the second portion.

In an aspect, a method of fabricating a positive active material may include preparing a first base aqueous solution which includes at least one of nickel, cobalt, manganese or aluminum, a second base aqueous solution of which a

concentration of at least one of nickel, cobalt, manganese or aluminum is different from that of the first base aqueous solution, and an additive aqueous solution including an additive metal, providing the first base aqueous solution, the second base aqueous solution and the additive aqueous solution into the reactor and adjusting a ratio of the first and second base aqueous solutions, thereby fabricating a positive active material precursor in which a metal hydroxide including at least one of nickel, cobalt, manganese, or aluminum is doped with the additive metal, and firing the positive active material precursor and lithium salt to fabricate a positive active material in which a metal oxide including lithium and at least one of nickel, cobalt, manganese or aluminum is doped with the additive metal. A doping concentration of the additive metal may be less than 2 mol %, and a concentration of at least one of nickel, cobalt, manganese or aluminum may be changed in a particle of the positive active material precursor.

In an embodiment, a firing temperature of the positive active material precursor and the lithium salt may be adjusted depending on the doping concentration of the additive metal.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view illustrating a positive active material according to some embodiments of the inventive concepts.

FIG. 2 is a cross-sectional view taken along a line A-B of FIG. 1.

FIG. 3 is a schematic view illustrating a positive active material according to a modified example of some embodiments of the inventive concepts.

FIG. 4 is a schematic view illustrating a primary particle included in a positive active material according to some embodiments of the inventive concepts.

FIG. 5(a) and FIG. 5(b) are an ASTAR image of a positive active material according to a comparative example 1, in black/white and color, respectively.

FIG. 6(a) and FIG. 6(b) are an ASTAR image of a positive active material according to an embodiment 7 of the inventive concepts, in black/white and color, respectively.

FIG. 7(a) and FIG. 7(b) show EDS mapping data (before charging/discharging) of the positive active material according to the comparative example 1, in black/white and color, respectively.

FIG. 8(a) and FIG. 8(b) show EDS mapping data (before charging/discharging) of the positive active material according to the embodiment 7 of the inventive concepts, in black/white and color, respectively.

FIG. 9(a) and FIG. 9(b) show EDS mapping data (after charging/discharging) of the positive active material according to the comparative example 1, in black/white and color, respectively.

FIG. 10(a) and FIG. 10(b) show EDS mapping data (after charging/discharging) of the positive active material according to the embodiment 7 of the inventive concepts, in black/white and color, respectively.

FIG. 11 shows SEM images of the positive active material according to the comparative example 1.

FIG. 12 shows SEM images of the positive active material according to the embodiment 7 of the inventive concepts.

FIG. 13 shows SEM images of the positive active material according to the embodiment 10 of the inventive concepts.

FIG. 14 is a XRD graph of positive active materials according to embodiments 2 and 7 of the inventive concepts and the comparative example 1.

FIG. 15 is a graph showing charge/discharge characteristics of positive active materials according to embodiments 2, 7, 10 and 12 of the inventive concepts and the comparative example 1.

FIG. 16 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 2, 7, 10 and 12 of the inventive concepts and the comparative example 1.

FIG. 17 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 7 of the inventive concepts and the comparative example 1.

FIG. 18 is an EIS measurement graph of the positive active material according to the comparative example 1.

FIG. 19 is an EIS measurement graph of the positive active material according to the embodiment 7 of the inventive concepts.

FIGS. 20 to 23 are graphs showing differential capacities of the positive active materials according to the embodiments 2, 7 and 10 of the inventive concepts and the comparative example 1.

FIG. 24 is a graph showing charge/discharge characteristics of positive active materials according to embodiments 1 to 4 of the inventive concepts and the comparative example 1.

FIG. 25 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 1 to 4 of the inventive concepts and the comparative example 1.

FIG. 26 is a graph showing charge/discharge characteristics of positive active materials according to embodiments 5 to 8 of the inventive concepts and the comparative example 1.

FIG. 27 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 5 to 8 of the inventive concepts and the comparative example 1.

FIG. 28 is a graph showing charge/discharge characteristics of positive active materials according to embodiments 9 to 11 of the inventive concepts and the comparative example 1.

FIG. 29 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 9 to 11 of the inventive concepts and the comparative example 1.

FIG. 30 is a graph showing charge/discharge characteristics of positive active materials according to the embodiments 2, 7 and 10 of the inventive concepts and comparative examples 1 to 5.

FIG. 31 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 2, 7 and 10 of the inventive concepts and the comparative examples 1 to 5.

FIG. 32 is a graph showing capacity retention characteristics of the positive active materials according to an embodiment 13 of the inventive concepts and a comparative example 6.

FIG. 33 is a graph showing an atomic ratio of a positive active material according to a comparative example 7.

FIG. 34 is a graph showing an atomic ratio of a positive active material according to an embodiment 14 of the inventive concepts.

FIG. 35 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 14 of the inventive concepts and the comparative example 7.

FIG. 36 is a graph showing capacity retention characteristics of the positive active materials according to an embodiment 15 of the inventive concepts and a comparative example 8.

FIG. 37 is a graph showing an atomic ratio of a positive active material precursor according to an embodiment 16 of the inventive concepts.

FIG. 38 is a graph showing an atomic ratio of a positive active material according to the embodiment 16 of the inventive concepts.

FIG. 39 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiment 16 of the inventive concepts and the comparative example 1.

FIG. 40 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 16 of the inventive concepts and the comparative example 1.

DETAILED DESCRIPTION OF THE EMBODIMENTS

The inventive concepts will now be described more fully hereinafter with reference to the accompanying drawings, in which exemplary embodiments of the inventive concepts are shown. It should be noted, however, that the inventive concepts are not limited to the following exemplary embodiments, and may be implemented in various forms. Accordingly, the exemplary embodiments are provided only to disclose the inventive concepts and let those skilled in the art know the category of the inventive concepts.

It will be understood that when an element such as a layer, region or substrate is referred to as being "on" another element, it can be directly on the other element or intervening elements may be present. In addition, in the drawings, the thicknesses of layers and regions are exaggerated for clarity.

It will be also understood that although the terms first, second, third etc. may be used herein to describe various elements, these elements should not be limited by these terms. These terms are only used to distinguish one element from another element. Thus, a first element in some embodiments could be termed a second element in other embodiments without departing from the teachings of the present invention. Exemplary embodiments of aspects of the present inventive concepts explained and illustrated herein include their complementary counterparts. As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

The terminology used herein is for the purpose of describing particular embodiments only and is not intended to limit the invention. As used herein, the singular terms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises", "comprising", "includes", "including", "have", "has" and/or "having" when used herein, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. Furthermore, it will be understood that when an element is referred to as being "connected" or "coupled" to another element, it may be directly connected or coupled to the other element or intervening elements may be present.

In addition, in explanation of the present invention, the descriptions to the elements and functions of related arts may be omitted if they obscure the subjects of the inventive concepts.

Moreover, it will be understood that when a ratio of a first crystal structure is higher than that of a second crystal structure in a specific portion, the specific portion may include both the first crystal structure and the second crystal structure and the ratio of the first crystal structure may be higher than that of the second crystal structure, or the specific portion may have only the first crystal structure.

Furthermore, in the present specification, a crystal system may include seven crystal systems, i.e., a triclinic crystal system, a monoclinic crystal system, an orthorhombic crystal system, a tetragonal crystal system, a trigonal or rhombohedral crystal system, a hexagonal crystal system, and a cubic crystal system.

Furthermore, the term "mol %" means a content of a metal included in a positive active material or positive active material precursor on the assumption that a sum of the other metals in the positive active material or positive active material precursor except lithium and oxygen is 100%.

FIG. 1 is a schematic view illustrating a positive active material according to some embodiments of the inventive concepts, FIG. 2 is a cross-sectional view taken along a line A-B of FIG. 1, and FIG. 3 is a schematic view illustrating a positive active material according to a modified example of some embodiments of the inventive concepts.

Referring to FIGS. 1 and 2, a positive active material **100** according to some embodiments of the inventive concepts may include lithium, an additive metal, and at least one of nickel, cobalt, manganese, or aluminum. In other words, the positive active material **100** may be an oxide which includes lithium, the additive metal, and at least one of nickel, cobalt, manganese, or aluminum. For example, the additive metal may be tungsten. For other examples, the additive metal may include at least one of tungsten, molybdenum, niobium, tantalum, titanium, zirconium, bismuth, ruthenium, magnesium, zinc, gallium, vanadium, chromium, calcium, strontium, or tin.

In some embodiments, the additive metal may include at least one of heavy metal elements having specific gravities of 4 or more. Alternatively, in other embodiments, the additive metal may include at least one of a group 4 element, a group 5 element, a group 6 element, a group 8 element, or a group 15 element.

When a content of the additive metal (e.g., tungsten) is 2 mol % or more in the positive active material **100**, capacity and life characteristics of the positive active material **100** may be deteriorated. Thus, according to some embodiments of the inventive concepts, the content of the additive metal (e.g., tungsten) of the positive active material **100** may be less than 2 mol %.

For an example, the positive active material **100** may be formed of a metal oxide including nickel, lithium, the additive metal, and oxygen. For another example, the positive active material **100** may be formed of a metal oxide including nickel, cobalt, lithium, the additive metal, and oxygen. For still another example, the positive active material **100** may be formed of a metal oxide including nickel, cobalt, manganese, lithium, the additive metal, and oxygen. For yet another example, the positive active material **100** may be formed of a metal oxide including nickel, cobalt, aluminum, lithium, the additive metal, and oxygen. The technical features according to embodiments of the inventive concepts may be applied to positive active materials including various materials.

In some embodiments, a concentration of the additive metal may be substantially constant in the positive active material **100**. Alternatively, in other embodiments, the positive active material **100** may include portions of which concentrations of the additive metal are different from each other, or the additive metal may have a concentration gradient in the positive active material **100**. In other words, the concentration of the additive metal may gradually increase or gradually decrease in a direction from a center toward a surface of the positive active material **100**. Alternatively, the additive metal may be mainly provided in a surface portion of the positive active material **100**, and thus the positive active material **100** may be divided into a core in which the concentration of the additive metal is relatively low, and a shell in which the concentration of the additive metal is relatively high.

In some embodiments, a concentration of at least one of nickel, cobalt, manganese, or aluminum may be substantially constant in the positive active material **100**. Alternatively, in other embodiments, at least one of nickel, cobalt, manganese, or aluminum may have a concentration gradient throughout a particle of the positive active material **100** in a direction from a center of the particle toward a surface of the particle or may have a concentration gradient in a portion of the particle in the direction. In still other embodiments, the positive active material **100** may include a core portion and a shell portion of which a concentration of a metal (at least one of nickel, cobalt, manganese, or aluminum) is different from that of the core portion. In yet other embodiments, a concentration gradient of at least one of nickel, cobalt, manganese, or aluminum may be changed in the particle (e.g., may increase and then decrease in the direction from the center toward the surface of the particle or may decrease and then increase in the direction). The technical features according to embodiments of the inventive concepts may be applied to positive active materials having various structures and shapes.

In some embodiments, the positive active material **100** may be represented by the following chemical formula 1.



In the chemical formula 1, each of 'M1', 'M2' and 'M3' is one of nickel, cobalt, manganese, and aluminum, $0 \leq a < 1$, $0 \leq b < 1$, $0 \leq c < 1$, $0 < d < 0.02$, at least one of 'a', 'b' or 'c' is greater than 0, and 'M1', 'M2', 'M3' and 'M4' are different metals from each other.

In the chemical formula 1, 'M4' may be the additive metal.

In some embodiments, a crystal structure may be controlled depending on the 'd' value (mol % of 'M4') in the chemical formula 1. In addition, the permeation amount of fluorine in a process of including the positive active material may be reduced depending on the 'd' value (mol % of 'M4') in the chemical formula 1 (this will be described later with reference to FIGS. 7 to 10).

The positive active material **100** may include a first crystal structure and a second crystal structure. The first crystal structure and the second crystal structure may be different crystal systems from each other. In some embodiments, the first crystal structure may be a cubic crystal structure, and the second crystal structure may be a trigonal or rhombohedral crystal structure. The crystal structure of the positive active material **100** may be checked or verified through an ASTAR image.

When the positive active material **100** includes a plurality of elements, the first crystal structure may be a cesium

chloride structure, a rock-salt structure, a zincblende structure, or a Weaire-Phelan structure.

The positive active material **100** may include a first portion **110** and a second portion **120**. The first portion **110** may be a portion of the positive active material **100**, in which a ratio of the first crystal structure is higher than that of the second crystal structure. The second portion **120** may be a portion of the positive active material **100**, in which a ratio of the second crystal structure is higher than that of the first crystal structure. Unlike FIG. 2, the first portion **110** and the second portion **120** may not be clearly distinguished from each other by a boundary.

As described above, in some embodiments, the first portion **110** may include both the first crystal structure and the second crystal structure, and the ratio of the first crystal structure may be higher than that of the second crystal structure in the first portion **110**. Alternatively, in other embodiments, the first portion **110** may have only the first crystal structure.

As described above, in some embodiments, the second portion **120** may include both the first crystal structure and the second crystal structure, and the ratio of the second crystal structure may be higher than that of the first crystal structure in the second portion **120**. Alternatively, in other embodiments, the second portion **120** may have only the second crystal structure.

The first portion **110** may surround at least a portion of the second portion **120**. For example, a thickness of the first portion **110** may be about 1 μm .

In some embodiments, the first portion **110** may completely surround the second portion **120** as illustrated in FIG. 2. In other words, the second portion **120** may be a core structure, and the first portion **110** may be a shell structure surrounding the core structure. That is, the positive active material **100** may have a core-shell structure having crystal systems which are crystallographically different from each other.

Alternatively, in other embodiments, the first portion **110** may surround a portion of the second portion **120** and the second portion **120** may form a portion of a surface of the positive active material **100**, as illustrated in FIG. 3.

As described above, the first portion **110** may be mainly located at an outer portion of the positive active material **100**, and the second portion **120** may be mainly located in an inner portion of the positive active material **100**. In some embodiments, the surface of the positive active material **100** and a portion of the positive active material **100** adjacent to the surface may mainly or completely have the cubic crystal structure, and a center of the positive active material **100** and a portion of the positive active material **100** adjacent to the center may mainly or completely have the trigonal or rhombohedral crystal structure. In other words, in the surface and the portion adjacent to the surface of the positive active material **100**, a ratio of the cubic crystal structure may be higher than that of the trigonal or rhombohedral crystal structure, or only the cubic crystal structure may be observed. In the center and the portion adjacent to the center of the positive active material **100**, a ratio of the trigonal or rhombohedral crystal structure may be higher than that of the cubic crystal structure, or only the trigonal or rhombohedral crystal structure may be observed.

In some embodiments, a ratio of the second portion **120** may be higher than that of the first portion **110** in the positive active material **100**. For example, a ratio of the second crystal structure may be higher than that of the first crystal structure in the positive active material **100**.

In the positive active material **100**, a portion having the first crystal structure (or the first portion **110**) and a portion having the second crystal structure (or the second portion **120**) may include the same material. For example, when the positive active material **100** is formed of an oxide including lithium, nickel, and tungsten, the portion having the first crystal structure (or the first portion **110**) and the portion having the second crystal structure (or the second portion **120**) may be formed of an oxide including lithium, nickel, and tungsten. For another example, when the positive active material **100** is formed of an oxide including lithium, nickel, cobalt, manganese, and tungsten, the portion having the first crystal structure (or the first portion **110**) and the portion having the second crystal structure (or the second portion **120**) may be formed of an oxide including lithium, nickel, cobalt, manganese, and tungsten.

In addition, in some embodiments, the portion having the first crystal structure (or the first portion **110**) and the portion having the second crystal structure (or the second portion **120**) may be represented by the same chemical formula. In other words, the portion having the first crystal structure (or the first portion **110**) and the portion having the second crystal structure (or the second portion **120**) may be chemically the same as each other.

As described above, according to the embodiments of the inventive concepts, the positive active material **100** may include the first portion **110** in which the ratio of the first crystal structure (e.g., the cubic crystal structure) is high, and the second portion **120** in which the ratio of the second crystal structure (e.g., the trigonal or rhombohedral crystal structure) is high and which is surrounded by the first portion **110**. Due to the first portion **110** in which the ratio of the first crystal structure is high, mechanical strength of the positive active material **100** may be improved and residual lithium of the surface of the positive active material **100** may be reduced. Thus, capacity, life span and thermal stability of a secondary battery including the positive active material **100** may be improved.

In addition, according to some embodiments, the ratios of the first crystal structure and the second crystal structure in the positive active material **100** may be adjusted depending on the content of the additive metal. For example, the ratio of the first crystal structure (e.g., the cubic crystal structure) may increase in the positive active material **100** as the content of the additive metal (e.g., tungsten) increases. When the content of the additive metal is 2 mol % or more, the ratio of the first crystal structure (e.g., the cubic crystal structure) may increase and the ratio of the second crystal structure (e.g., the trigonal or rhombohedral crystal structure) may decrease. Thus, a movement path of lithium ions may be reduced in the secondary battery including the positive active material **100**. Therefore, when the content of the additive metal (e.g., tungsten) is 2 mol % or more, charge/discharge characteristics of the secondary battery including the positive active material **100** may be deteriorated.

However, according to the aforementioned embodiments of the inventive concepts, the content of the additive metal may be less than 2 mol %, and thus the charge/discharge characteristics of the secondary battery including the positive active material **100** may be improved.

FIG. 4 is a schematic view illustrating a primary particle included in a positive active material according to some embodiments of the inventive concepts.

Referring to FIG. 4, according to some embodiments, the positive active material may include primary particles **30** and a secondary particle in which the primary particles **30** are aggregated.

The primary particles **30** may extend in directions radiating from one region of the inside of the secondary particle toward a surface **20** of the secondary particle. The one region of the inside of the secondary particle may be a center **10** of the secondary particle. In other words, the primary particle **30** may have a rod shape which extends from the one region of the inside of the secondary particle toward the surface **20** of the secondary particle.

A movement path of metal ions (e.g., lithium ions) and an electrolyte may be provided between the primary particles **30** having the rod shapes, i.e., between the primary particles **30** extending in directions D from the center **10** toward the surface **20** of the secondary particle. Thus, the positive active material according to the embodiments of the inventive concepts may improve charge/discharge efficiency of a secondary battery.

According to some embodiments, the primary particle **30** relatively adjacent to the surface **20** of the secondary particle may have a longer length in the direction from the center **10** toward the surface **20** of the secondary particle than the primary particle **30** relatively adjacent to the center **10** of the secondary particle. In other words, in at least a portion of the secondary particle which extends from the center **10** to the surface **20** of the secondary particle, the lengths of the primary particles **30** may sequentially increase as a distance from the surface **20** of the secondary particle decreases.

In some embodiments, when the positive active material **100** includes the additive metal as described with reference to FIGS. 1 to 3, contents of the additive metal in the primary particles **30** may be substantially equal to each other. For example, the content of the additive metal in the primary particles **30** may be less than 2 mol %.

In addition, as described with reference to FIGS. 1 to 3, the positive active material according to some embodiments of the inventive concepts may have the first crystal structure and the second crystal structure. Thus, some of the primary particles **30** may have both the first crystal structure and the second crystal structure. In addition, others of the primary particles **30** may have only the first crystal structure or may have only the second crystal structure. In this case, according to some embodiments, a ratio of the primary particles **30** having the first crystal structure (e.g., the cubic crystal structure) may increase as a distance from the surface **20** of the positive active material decreases, and a ratio of the primary particles **30** having the second crystal structure (e.g., the trigonal or rhombohedral crystal structure) may increase as a distance from the center **10** of the positive active material decreases.

A method of fabricating a positive active material according to some embodiments of the inventive concepts will be described hereinafter.

A first base aqueous solution, a second base aqueous solution, and an additive aqueous solution may be prepared. The first base aqueous solution may include at least one of nickel, cobalt, manganese, or aluminum. A concentration of at least one of nickel, cobalt, manganese, or aluminum of the second base aqueous solution may be different from that of the first base aqueous solution. The additive aqueous solution may include an additive metal.

In some embodiments, the preparation of the additive aqueous solution may include preparing a source including the additive metal, and forming the additive aqueous solution by dissolving the source in a solvent. For example,

when the additive metal is tungsten, the source may be tungsten oxide (WO₃). For example, the solvent may include NaOH.

In some embodiments, the formation of the additive aqueous solution may include dissolving the source (e.g., tungsten oxide) in LiOH, and forming the additive aqueous solution by mixing the solvent with LiOH in which the source is dissolved. Thus, the source may be easily dissolved.

In some embodiments, the formation of the additive aqueous solution may include forming a first additive metal aqueous solution in which a concentration of the additive metal is relatively high, and forming a second additive metal aqueous solution in which a concentration of the additive metal is relatively low. The additive metal may have a concentration gradient in a positive active material by using the first additive metal aqueous solution and the second additive metal aqueous solution, as described later.

The solvent may not only dissolve the source but also adjust a pH in a reactor in a process of fabricating a positive active material precursor using the additive aqueous solution as described later.

When the first and second base aqueous solutions include nickel, the first and second base aqueous solutions may include, for example, nickel sulfate. When the first and second base aqueous solutions include cobalt, the first and second base aqueous solutions may include, for example, cobalt sulfate. When the first and second base aqueous solutions include manganese, the first and second base aqueous solutions may include, for example, manganese sulfate. When the first and second base aqueous solutions include at least two of nickel, cobalt, manganese, or aluminum, the first and second base aqueous solutions may include at least two metal salt aqueous solutions.

The first base aqueous solution, the second base aqueous solution, and the additive aqueous solution may be provided into the reactor and a ratio of the first and second base aqueous solutions may be adjusted, thereby fabricating a positive active material precursor in which a metal hydroxide including at least one of nickel, cobalt, manganese, or aluminum is doped with the additive metal. In addition to the first and second base aqueous solutions and the additive aqueous solution, an ammonia solution may further be provided into the reactor. The pH in the reactor may be adjusted by a supply amount of the ammonia solution and the solvent in which the additive metal is dissolved.

In some embodiments, when the first additive metal aqueous solution and the second additive metal aqueous solution are formed as described above, the additive metal may have a concentration gradient in the positive active material precursor by adjusting a ratio of the first and second additive metal aqueous solutions of which the concentrations of the additive metal are different from each other.

Since the ratio of the first and second base aqueous solutions is adjusted as described above, a concentration of at least one of nickel, cobalt, manganese, or aluminum may be changed or varied in a particle of the positive active material precursor.

In other embodiments, the source including the additive metal may be dissolved in the first and second base aqueous solutions and then may be provided into the reactor.

For example, when the first and second base aqueous solutions include nickel and the additive metal is tungsten, the positive active material precursor may be represented by the following chemical formula 2. In the following chemical formula 2, 'x' may be less than 1 and greater than 0.



In other embodiments, when the second base aqueous solution has a lower nickel concentration, a higher cobalt concentration, and a higher manganese concentration than the first base aqueous solution, the positive active material precursor may be fabricated by gradually increasing a ratio of the second base aqueous solution to the first base aqueous solution having the relatively high nickel concentration and the relatively low cobalt and manganese concentrations. In this case, in the particle of the positive active material precursor, a concentration of nickel may gradually decrease in a direction from a center toward a surface of the particle and concentrations of cobalt and manganese may gradually increase in the direction.

The positive active material precursor and lithium salt may be fired to fabricate a positive active material in which a metal oxide including lithium and at least one of nickel, cobalt, manganese, or aluminum is doped with the additive metal.

For example, when the first and second base aqueous solutions include nickel and the additive metal is tungsten as described above, the positive active material may be represented by the following chemical formula 3.



In some embodiments, a firing temperature of the positive active material precursor and the lithium salt may be adjusted depending on a doping concentration of the additive metal. For example, the firing temperature of the positive active material precursor and the lithium salt may increase as the doping concentration of the additive metal increases. For example, when the doping concentration of the additive metal is 0.5 mol %, the firing temperature of the positive active material precursor and the lithium salt may be about 730° C. When the doping concentration of the additive metal is 1.0 mol %, the firing temperature of the positive active material precursor and the lithium salt may be about 760° C. When the doping concentration of the additive metal is 1.5 mol %, the firing temperature of the positive active material precursor and the lithium salt may be about 790° C.

Unlike the embodiments of the inventive concepts, if the firing temperature of the positive active material precursor and the lithium salt is not adjusted depending on the doping concentration of the additive metal, charge/discharge characteristics of a secondary battery including a fabricated positive active material may be deteriorated.

However, according to the aforementioned embodiments of the inventive concepts, the firing temperature of the positive active material precursor and the lithium salt may be adjusted depending on the doping concentration of the additive metal, and thus the charge/discharge characteristics of the secondary battery including the positive active material may be improved.

Evaluation results of characteristics of the positive active material according to the aforementioned embodiments of the inventive concepts will be described hereinafter.

Fabrication of Positive Active Materials According to Embodiments 1 to 4

WO₃ powder was dissolved at a concentration of 0.235M in 0.4 L of a 1.5M lithium hydroxide solution. The formed solution was dissolved in 9.6 L of a 4M sodium hydroxide solution to form an additive aqueous solution in which tungsten (W) was dissolved. 10 liters of distilled water was provided into a co-precipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min,

and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A 2M nickel sulfate aqueous solution and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 15 hours to 35 hours. In addition, the additive aqueous solution was supplied into the reactor to adjust a pH and to add tungsten, and thus a metal composite hydroxide ($\text{Ni}_{0.995}\text{W}_{0.005}(\text{OH})_2$) was formed.

The formed metal composite hydroxide ($\text{Ni}_{0.995}\text{W}_{0.005}(\text{OH})_2$) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide ($\text{Ni}_{0.995}\text{W}_{0.005}(\text{OH})_2$) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 710° C. for 10 hours to fabricate positive active material ($\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$) powder according to an embodiment 1.

In the method described in the above embodiment 1, the metal composite hydroxide ($\text{Ni}_{0.995}\text{W}_{0.005}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 730° C. to fabricate positive active material ($\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$) powder according to an embodiment 2.

In the method described in the above embodiment 1, the metal composite hydroxide ($\text{Ni}_{0.995}\text{W}_{0.005}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 750° C. to fabricate positive active material ($\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$) powder according to an embodiment 3.

In the method described in the above embodiment 1, the metal composite hydroxide ($\text{Ni}_{0.995}\text{W}_{0.005}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 770° C. to fabricate positive active material ($\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$) powder according to an embodiment 4.

TABLE 1

Classification	Positive active material	Firing temperature
Embodiment 1	$\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$	710° C.
Embodiment 2	$\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$	730° C.
Embodiment 3	$\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$	750° C.
Embodiment 4	$\text{LiNi}_{0.995}\text{W}_{0.005}\text{O}_2$	770° C.

Fabrication of Positive Active Materials According to Embodiments 5 to 8

In the method described in the above embodiment 1, the WO_3 powder was dissolved at a concentration of 0.47M to form an additive aqueous solution, a metal composite hydroxide ($\text{Ni}_{0.99}\text{W}_{0.01}(\text{OH})_2$) was formed using this additive aqueous solution, and the metal composite hydroxide and lithium hydroxide (LiOH) were fired at 730° C. to fabricate positive active material ($\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$) according to an embodiment 5.

In the method described in the above embodiment 5, the metal composite hydroxide ($\text{Ni}_{0.99}\text{W}_{0.01}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 750° C. to fabricate positive active material ($\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$) powder according to an embodiment 6.

In the method described in the above embodiment 5, the metal composite hydroxide ($\text{Ni}_{0.99}\text{W}_{0.01}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 760° C. to fabricate positive active material ($\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$) powder according to an embodiment 7.

In the method described in the above embodiment 5, the metal composite hydroxide ($\text{Ni}_{0.99}\text{W}_{0.01}(\text{OH})_2$) and lithium

hydroxide (LiOH) were fired at 770° C. to fabricate positive active material ($\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$) powder according to an embodiment 8.

TABLE 2

Classification	Positive active material	Firing temperature
Embodiment 5	$\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$	730° C.
Embodiment 6	$\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$	750° C.
Embodiment 7	$\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$	760° C.
Embodiment 8	$\text{LiNi}_{0.99}\text{W}_{0.01}\text{O}_2$	770° C.

Fabrication of Positive Active Materials According to Embodiments 9 to 11

In the method described in the above embodiment 1, the WO_3 powder was dissolved at a concentration of 0.705M to form an additive aqueous solution, a metal composite hydroxide ($\text{Ni}_{0.985}\text{W}_{0.015}(\text{OH})_2$) was formed using this additive aqueous solution, and the metal composite hydroxide and lithium hydroxide (LiOH) were fired at 770° C. to fabricate positive active material ($\text{LiNi}_{0.985}\text{W}_{0.015}\text{O}_2$) according to an embodiment 9.

In the method described in the above embodiment 9, the metal composite hydroxide ($\text{Ni}_{0.985}\text{W}_{0.015}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 790° C. to fabricate positive active material ($\text{LiNi}_{0.985}\text{W}_{0.015}\text{O}_2$) powder according to an embodiment 10.

In the method described in the above embodiment 9, the metal composite hydroxide ($\text{Ni}_{0.985}\text{W}_{0.015}(\text{OH})_2$) and lithium hydroxide (LiOH) were fired at 810° C. to fabricate positive active material ($\text{LiNi}_{0.985}\text{W}_{0.015}\text{O}_2$) powder according to an embodiment 11.

TABLE 3

Classification	Positive active material	Firing temperature
Embodiment 9	$\text{LiNi}_{0.985}\text{W}_{0.015}\text{O}_2$	770° C.
Embodiment 10	$\text{LiNi}_{0.985}\text{W}_{0.015}\text{O}_2$	790° C.
Embodiment 11	$\text{LiNi}_{0.985}\text{W}_{0.015}\text{O}_2$	810° C.

Fabrication of Positive Active Material According to Embodiment 12

In the method described in the above embodiment 1, the WO_3 powder was dissolved at a concentration of 0.94M to form an additive aqueous solution, a metal composite hydroxide ($\text{Ni}_{0.98}\text{W}_{0.02}(\text{OH})_2$) was formed using this additive aqueous solution, and the metal composite hydroxide and lithium hydroxide (LiOH) were fired at 790° C. to fabricate positive active material ($\text{LiNi}_{0.98}\text{W}_{0.02}\text{O}_2$) according to an embodiment 12.

Fabrication of Positive Active Material According to Comparative Example 1

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N_2 gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A 2M nickel sulfate aqueous solution and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 15 hours to 35 hours. In addition, a sodium hydroxide solution was supplied into the reactor to adjust a pH, and thus a metal composite hydroxide ($\text{Ni}(\text{OH})_2$) was formed.

The formed metal composite hydroxide ($\text{Ni}(\text{OH})_2$) was filtered, was cleaned by water, and then, was dried in a

vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni(OH)₂) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 650° C. for 10 hours to fabricate positive active material (LiNiO₂) powder according to a comparative example 1.

The positive active materials according to the embodiments 1 to 12 and the comparative example 1 may be listed as the following table 1.

TABLE 4

Classification	Positive active material
Comparative example 1	LiNiO ₂
Embodiments 1 to 4	LiNi _{0.995} W _{0.005} O ₂
Embodiments 5 to 8	LiNi _{0.99} W _{0.01} O ₂
Embodiments 9 to 11	LiNi _{0.985} W _{0.015} O ₂
Embodiment 12	LiNi _{0.98} W _{0.02} O ₂

Residual lithium according to the embodiment 8 of the inventive concepts and residual lithium according to the comparative example 1 were measured as shown in the following table 5.

TABLE 5

Classification	LiOH (ppm)	Li ₂ CO ₃ (ppm)	Total Residual Li (ppm)
Comparative example 1	17822.4	8128.8	25951.2
Embodiment 8	16497.7	3516.0	20013.6

As shown in the table 5, the amount of the residual lithium of the positive active material according to the embodiment 8 is less than the amount of the residual lithium of the positive active material according to the comparative example 1 by about 6000 ppm.

FIG. 5(a) and FIG. 5(b) are an ASTAR image of a positive active material according to the comparative example 1, and FIG. 6(a) and FIG. 6(b) are an ASTAR image of a positive active material according to the embodiment 7 of the inventive concepts.

Referring to FIGS. 5(a), 5(b), 6(a), and 6(b), ASTAR images of the positive active materials according to the comparative example 1 and the embodiment 7 were obtained. In FIGS. 5(a), 5(b), 6(a), and 6(b), a black region shows the trigonal or rhombohedral crystal structure, and a gray region shows the cubic crystal structure.

As shown in FIGS. 5(a), 5(b), 6(a), and 6(b), in the positive active material according to the comparative example 1, the cubic crystal structure and the trigonal or rhombohedral crystal structure are uniformly and randomly distributed. On the contrary, in the positive active material according to the embodiment 7, the cubic crystal structure is mainly distributed in a surface portion of the positive active material and the trigonal or rhombohedral crystal structure is mainly distributed within the positive active material. In other words, a first portion in which a ratio of the cubic crystal structure is higher than that of the trigonal or rhombohedral crystal structure surrounds at least a portion of a second portion in which a ratio of the trigonal or rhombohedral crystal structure is higher than that of the cubic crystal structure.

FIG. 7(a) and FIG. 7(b) show EDS mapping data (before charging/discharging) of the positive active material according to the comparative example 1, and FIG. 8(a) and FIG.

8(b) show EDS mapping data (before charging/discharging) of the positive active material according to the embodiment 7 of the inventive concepts. FIG. 9(a) and FIG. 9(b) show EDS mapping data (after charging/discharging) of the positive active material according to the comparative example 1, and FIG. 10(a) and FIG. 10(b) show EDS mapping data (after charging/discharging) of the positive active material according to the embodiment 7 of the inventive concepts.

Referring to FIGS. 7(a), 7(b), 8(a), and 8(b), tungsten which is the additive metal is substantially uniformly distributed in a particle of the positive active material according to the embodiment 7 of the inventive concepts.

In addition, referring to FIGS. 9(a), 9(b), 10(a), and 10(b), in the positive active material according to the comparative example 1 which does not include the additive metal, fluorine (F) existing in an electrolyte permeates into a particle in a charge/discharge operation. On the contrary, in the positive active material according to the embodiment 7 which includes the additive metal (i.e., tungsten), a very small amount of fluorine (F) which is much less than that of the comparative example 1 permeates into the particle. In other words, when the positive active material including the additive metal (e.g., tungsten) is fabricated according to the embodiments of the inventive concepts, fluorine (F) permeating in the charge/discharge operation may be minimized, and thus life and capacity characteristics of the positive active material may be improved.

FIG. 11 shows SEM images of the positive active material according to the comparative example 1, FIG. 12 shows SEM images of the positive active material according to the embodiment 7 of the inventive concepts, and FIG. 13 shows SEM images of the positive active material according to the embodiment 10 of the inventive concepts. FIG. 14 is a XRD graph of positive active materials according to embodiments 2 and 7 of the inventive concepts and the comparative example 1.

Referring to FIGS. 11 to 14, SEM images of the positive active materials according to the comparative example 1 and the embodiments 7 and 10 were obtained. As shown in FIGS. 11 to 13, a plurality of particles of the positive active material according to the comparative example 1 are broken after 100 cycles of charging/discharging. However, the positive active materials according to the embodiments 7 and 10 have stabilized crystal structures, and thus breakage of particles thereof may be minimized.

FIG. 15 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiments 2, 7, 10 and 12 of the inventive concepts and the comparative example 1, and FIG. 16 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 2, 7, 10 and 12 of the inventive concepts and the comparative example 1.

Referring to FIGS. 15 and 16, half cells were manufactured using the positive active materials according to the embodiments 2, 7, 10 and 12 and the comparative example 1. Discharge capacities of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.1 C, and 30° C., and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C. The measured results are shown in FIGS. 15 and 16 and the following table 6.

TABLE 6

	0.1 C, 1st Dis-Capa (mAh/g)	1st Efficiency	0.2 C Capacity (mAh/g)	0.2 C/0.1 C	0.5 C Capacity (mAh/g)	0.5 C/0.1 C	Cycle number	0.5 C Cycle Retention
Comparative example 1	247.5	96.8%	242.3	97.9%	232.5	93.9%	100	73.7%
Embodiment 2	246.7	96.1%	242.5	98.3%	233.1	94.5%	100	83.2%
Embodiment 7	244.0	95.6%	240.0	98.4%	233.2	95.6%	100	88.2%
Embodiment 10	240.8	94.9%	235.4	97.8%	226.6	94.1%	100	89.8%
Embodiment 12	201.4	96.0%	182.5	90.6%	160.7	79.8%	15	98.4%

As shown in FIGS. 15 and 16 and the table 6, discharge capacity and life characteristics of the secondary batteries manufactured using the positive active materials according to the embodiments 2, 7, 10 and 12 are significantly superior to those of the secondary battery manufactured using the positive active material according to the comparative example 1. In addition, in the case of the positive active material according to the embodiment 12, discharge capacity characteristics are significantly reduced due to an excessive amount of tungsten. Thus, it may be recognized that the content of the additive metal in the positive active material is controlled less than 2 mol % to effectively improve the capacity characteristics of the secondary battery.

FIG. 17 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 7 of the inventive concepts and the comparative example 1.

Referring to FIG. 17, discharge capacities according to the number of charge/discharge cycles of the positive active materials according to the embodiment 7 and the comparative example 1 were measured. The measured results are shown in FIG. 17 and the following table 7.

TABLE 7

Classification	1st Discharge Capacity at 0.1 C (mAhg ⁻¹)		0.2 C (mAhg ⁻¹) (0.2 C/0.1 C)	0.5 C (mAhg ⁻¹) (0.5 C/0.1 C)	1 C (mAhg ⁻¹) (1 C/0.1 C)	2 C (mAhg ⁻¹) (2 C/0.1 C)	5 C (mAhg ⁻¹) (5 C/0.1 C)
	1st Ah Efficiency						
Comparative example 1	245.0	97.3%	239.2 (97.6%)	232.7 (95.0%)	225.0 (91.9%)	215.1 (87.8%)	201.0 (82.1%)
Embodiment 7	243.5	95.9%	240.0 (98.7%)	234.0 (96.2%)	225.3 (92.6%)	215.9 (88.8%)	206.1 (84.7%)

As shown in FIG. 17 and the table 7, life characteristics of the secondary battery manufactured using the positive active material according to the embodiment 7 are superior to those of the secondary battery manufactured using the positive active material according to the comparative example 1.

FIG. 18 is an electrochemical impedance spectroscopy (EIS) measurement graph of the positive active material according to the comparative example 1, and FIG. 19 is an EIS measurement graph of the positive active material according to the embodiment 7 of the inventive concepts.

Referring to FIGS. 18 and 19, secondary batteries including the positive active materials according to the comparative example 1 and the embodiment 7 were manufactured, and electrochemical impedances according to a charge/discharge cycle thereof were measured.

TABLE 8

Classification	Resistance (Ω)	Cycle			
		1st	25th	50th	100th
Comparative example 1	Rsf	6.9	7	7.2	9.4
	Rct	6.5	12.5	25.5	70.2
Embodiment 7	Rsf	6.1	6.4	6.8	7.3
	Rct	6.3	11.3	14.7	22.1

As shown in FIGS. 18 and 19 and the table 8, Rsf values and Rct values of the positive active material including the additive metal (tungsten) according to the embodiment 7 are significantly lower than those of the positive active material according to the comparative example 1. In addition, it may be recognized that a difference therebetween gradually increases as the number of the charge/discharge cycles increases. In other words, it may be recognized that a surface of the positive active material including the additive metal (tungsten) according to the embodiment 7 is more stable than a surface of the positive active material according to the comparative example 1.

FIGS. 20 to 23 are graphs showing differential capacities of the positive active materials according to the embodiments 2, 7 and 10 of the inventive concepts and the comparative example 1.

Referring to FIGS. 20 and 23, half cells were manufactured using the positive active materials according to the embodiments 2, 7 and 10 and the comparative example 1, and differential capacities of the half cells were measured. As shown in FIGS. 20 to 23, phase transition rates of the positive active materials according to the embodiments 2, 7 and 10 are much lower than that of the positive active material according to the comparative example 1. In addition, in the cases of the positive active materials according to the embodiments 7 and 10, a H1 Phase is still shown after 100 cycles.

FIG. 24 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiments 1 to 4 of the inventive concepts and the comparative example 1, and FIG. 25 is a graph showing capacity retention characteristics of the positive active mate-

rials according to the embodiments 1 to 4 of the inventive concepts and the comparative example 1.

Half cells were manufactured using the positive active materials according to the embodiments 1 to 4 and the comparative example 1. Discharge capacities of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.1 C, and 30° C., and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C. The measured results are shown in FIGS. 24 and 25 and the following table 9.

TABLE 9

	0.1 C, 1st Dis-Capa (mAh/g)	1st Efficiency	0.2 C Capacity (mAh/g)	0.2 C/0.1 C	0.5 C Capacity (mAh/g)	0.5 C/0.1 C	Cycle number	0.5 C Cycle Retention
Comparative example 1	247.5	96.8%	242.3	97.9%	232.5	93.9%	100	73.7%
Embodiment 1	243.9	96.0%	239.0	98.0%	229.3	94.0%	100	75.2%
Embodiment 2	246.7	96.1%	242.5	98.3%	233.1	94.5%	100	83.2%
Embodiment 3	247.7	96.5%	241.4	97.5%	230.5	93.1%	100	80.8%
Embodiment 4	239.3	93.8%	236.7	98.9%	224.5	93.8%	100	80.5%

As shown in FIGS. 24 and 25 and the table 9, discharge capacity and life characteristics of the secondary batteries manufactured using the positive active materials according to the embodiments 1 to 4 are significantly superior to those of the secondary battery manufactured using the positive active material according to the comparative example 1. In addition, the firing temperatures of the positive active material precursor and the lithium salt in the embodiments 1 to 4 doped with the additive metal are higher than that in the comparative example 1 not doped with the additive metal. Furthermore, it may be recognized that the charge/discharge characteristics are effectively improved by controlling the firing temperature of the positive active material precursor and the lithium salt to about 730° C., like the embodiment 2.

FIG. 26 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiments 5 to 8 of the inventive concepts and the comparative example 1, and FIG. 27 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 5 to 8 of the inventive concepts and the comparative example 1.

Half cells were manufactured using the positive active materials according to the embodiments 5 to 8 and the comparative example 1. Discharge capacities of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.1 C, and 30° C., and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C. The measured results are shown in FIGS. 26 and 27 and the following table 10.

TABLE 10

	0.1 C, 1st Dis-Capa (mAh/g)	1st Efficiency	0.2 C Capacity (mAh/g)	0.2 C/0.1 C	0.5 C Capacity (mAh/g)	0.5 C/0.1 C	Cycle number	0.5 C Cycle Retention
Comparative example 1	247.5	96.8%	242.3	97.9%	232.5	93.9%	100	73.7%
Embodiment 5	242.1	96.0%	236.1	97.5%	226.1	93.4%	100	87.6%
Embodiment 6	238.1	95.1%	233.9	98.2%	226.5	95.1%	100	88.6%
Embodiment 7	244.0	95.6%	240.0	98.4%	233.2	95.6%	100	88.2%
Embodiment 8	245.0	95.6%	241.7	98.6%	234.9	95.9%	100	86.5%

As shown in FIGS. 26 and 27 and the table 10, discharge capacity and life characteristics of the secondary batteries manufactured using the positive active materials according to the embodiments 5 to 8 are significantly superior to those of the secondary battery manufactured using the positive active material according to the comparative example 1. In addition, the firing temperatures of the positive active material precursor and the lithium salt in the embodiments 5 to 8 doped with the additive metal are higher than that in the

comparative example 1 not doped with the additive metal. Furthermore, when the content of the additive metal increases to 1.0 mol % as compared with the embodiments 1 to 4 (the content of the additive metal: 0.5 mol %), the firing temperature of the positive active material precursor and the lithium salt increases to effectively improve charge/discharge efficiency.

FIG. 28 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiments 9 to 11 of the inventive concepts and the comparative example 1, and FIG. 29 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 9 to 11 of the inventive concepts and the comparative example 1.

Half cells were manufactured using the positive active materials according to the embodiments 9 to 11 and the comparative example 1. Discharge capacities of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.1 C, and 30° C., and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C. The measured results are shown in FIGS. 28 and 29 and the following table 11.

TABLE 11

	0.1 C, 1st Dis-Capa (mAh/g)	1st Efficiency	0.2 C Capacity (mAh/g)	0.2 C/0.1 C	0.5 C Capacity (mAh/g)	0.5 C/0.1 C	Cycle number	0.5 C Cycle Retention
Comparative example 1	247.5	96.8%	242.3	97.9%	232.5	93.9%	100	73.7%
Embodiment 9	238.7	95.3%	231.8	97.1%	221.2	92.7%	100	92.1%
Embodiment 10	240.8	94.9%	235.4	97.8%	226.6	94.1%	100	89.8%
Embodiment 11	240.9	95.0%	236.1	98.0%	227.6	94.5%	100	89.8%

As shown in FIGS. 28 and 29 and the table 11, the firing temperatures of the positive active material precursor and the lithium salt in the embodiments 9 to 11 doped with the additive metal are higher than that in the comparative example 1 not doped with the additive metal. In addition, when the content of the additive metal increases to 1.5 mol % as compared with the embodiments 1 to 4 (the content of the additive metal: 0.5 mol %) and the embodiments 5 to 8 (the content of the additive metal: 1.0 mol %), the firing temperature of the positive active material precursor and the lithium salt increases to effectively improve the charge/discharge efficiency.

Fabrication of Positive Active Materials According to Comparative Examples 2 and 3

A metal composite hydroxide (Ni(OH)₂) was formed by performing the same process as the comparative example 1 described above.

The formed metal composite hydroxide (Ni(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. The metal composite hydroxide (Ni(OH)₂) and WO₃ powder were mixed with each other at a molar ratio of 99.5:0.5, and then, the mixture was mixed with lithium hydroxide (LiOH). Thereafter, the mixture mixed with lithium hydroxide (LiOH) was fired at 650° C. to fabricate positive active material (LiNi_{0.995}W_{0.005}O₂) powder according to a comparative example 2.

In the method described in the above comparative example 2, the metal composite hydroxide (Ni(OH)₂) and the WO₃ powder were mixed with each other at a molar ratio of 99:1. Thus, positive active material (LiNi_{0.99}W_{0.01}O₂) powder according to a comparative example 3 was fabricated.

Fabrication of Positive Active Materials According to Comparative Examples 4 and 5

LiNiO₂ powder was formed by performing the same process as the comparative example 1 described above.

The formed LiNiO₂ powder and WO₃ were mixed with each other at a molar ratio of 99.75:0.25, and the mixture

was ball-milled. Thereafter, the ball-milled mixture was thermally treated at 400° C. to fabricate positive active material (W coating 0.25 mol % LiNiO₂) powder according to a comparative example 4.

In the method described in the above comparative example 4, LiNiO₂ powder and WO₃ were mixed with each other at a molar ratio of 99.5:0.5, and the mixture was ball-milled. Thereafter, the ball-milled mixture was thermally treated at 400° C. to fabricate positive active material (W coating 0.5 mol % LiNiO₂) powder according to a comparative example 5.

The positive active materials according to the comparative examples 2 to 4 may be listed as the following table 10.

TABLE 12

Classification	Positive active material
Comparative example 2	WO ₃ 0.5 mol %
Comparative example 3	WO ₃ 1.0 mol %
Comparative example 4	W coating 0.25 mol %
Comparative example 5	W coating 0.5 mol %

FIG. 30 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiments 2, 7 and 10 of the inventive concepts and the comparative examples 1 to 5, and FIG. 31 is a graph showing capacity retention characteristics of the positive active materials according to the embodiments 2, 7 and 10 of the inventive concepts and the comparative examples 1 to 5.

Referring to FIGS. 30 and 31, half cells were manufactured using the positive active materials according to the comparative examples 2 to 5. Discharge capacities of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.1 C, and 30° C., and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C. The measured results are shown in FIGS. 30 and 31 and the following table 13.

TABLE 13

	0.1 C, 1st Dis-Capa (mAh/g)	1st Efficiency	0.2 C Capacity (mAh/g)	0.2 C/ 0.1 C	0.5 C Capacity (mAh/g)	0.5 C/0.1 C	Cycle number	0.5 C Cycle Retention
Comparative example 2	246.9	97.1	242.2	98.1	233.8	94.7	100	76.7
Comparative example 3	242.0	97.2	235.5	97.3	224.6	92.8	100	79.6
Comparative example 4	247.5	97.6	242.2	97.9	233.1	94.2	58	88.8
Comparative example 5	247.3	97.7	241.8	97.7	232.3	93.9	59	87.9

As shown in FIGS. 30 and 31 and the tables 8 and 13, the discharge capacity and life characteristics of the secondary batteries manufactured using the positive active materials including the additive metal according to the embodiments are significantly superior to those of the secondary batteries manufactured using the positive active materials according to the comparative examples 1 to 5.

Fabrication of Positive Active Material According to Embodiment 13

WO₃ powder was dissolved at a concentration of 0.28M in 0.4 L of a 1.5M lithium hydroxide solution. The formed solution was dissolved in 9.6 L of a 4M sodium hydroxide solution to form 10 L of a first additive metal aqueous solution in which tungsten (W) was dissolved.

In addition, WO₃ powder was dissolved at a concentration of 0.56M in 0.2 L of a 1.5M lithium hydroxide solution. The formed solution was dissolved in 4.8 L of a 4M sodium hydroxide solution to form 5 L of a second additive metal aqueous solution in which tungsten (W) was dissolved.

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A first base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=90:5:5) and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 15 hours to 35 hours while mixing a second base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=57:16:27) with the first base aqueous solution at 0.561 liter/hour. In addition, the first and second additive metal aqueous solutions were supplied into the reactor to adjust a pH and to add tungsten while mixing the second additive metal aqueous solution with the first additive metal aqueous solution at 0.561 liter/hour, thereby forming a metal composite hydroxide (Ni_{0.646}Co_{0.129}Mn_{0.218}W_{0.007}(OH)₂).

The formed metal composite hydroxide (Ni_{0.646}Co_{0.129}Mn_{0.218}W_{0.007}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni_{0.646}Co_{0.129}Mn_{0.218}W_{0.007}(OH)₂) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 820° C. for 10 hours to fabricate positive active material (LiNi_{0.646}Co_{0.129}Mn_{0.218}W_{0.007}O₂) powder according to an embodiment 13.

Fabrication of Positive Active Material According to Comparative Example 6

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A first base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=90:5:5) and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 15 hours to 35 hours while mixing a second base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (con-

centration: 2M, molar ratio of nickel:cobalt:manganese=57:16:27) with the first base aqueous solution at 0.561 liter/hour. In addition, a sodium hydroxide solution was supplied to adjust a pH.

A formed metal composite hydroxide (Ni_{0.65}Co_{0.13}Mn_{0.22}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni_{0.65}Co_{0.13}Mn_{0.22}(OH)₂) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 820° C. for 10 hours to fabricate positive active material (LiNi_{0.65}Co_{0.13}Mn_{0.22}O₂) powder according to a comparative example 6.

FIG. 32 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 13 of the inventive concepts and the comparative example 6.

Referring to FIG. 32, half cells were manufactured using the positive active materials according to the embodiment 13 and the comparative example 6, and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C.

As shown in FIG. 32, capacity and charge/discharge characteristics of the embodiment 13 doped with the additive metal are superior to those of the comparative example 6 not doped with the additive metal.

Fabrication of Positive Active Material According to Embodiment 14

WO₃ powder was dissolved at a concentration of 0.24M in 0.4 L of a 1.5M lithium hydroxide solution. The formed solution was dissolved in 9.6 L of a 4M sodium hydroxide solution to form 10 L of an additive aqueous solution in which tungsten (W) was dissolved.

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A first base aqueous solution including nickel sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:manganese=98:2) and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 5 hours to 15 hours while mixing a second base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=80:8:12) with the first base aqueous solution at 0.561 liter/hour. In addition, continuously, the first base aqueous solution and the 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 10 hours to 20 hours while mixing a third base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=72:6:22) with the first and second base aqueous solutions at 0.561 liter/hour. In addition, the additive aqueous solution was supplied into the reactor to adjust a pH and to add tungsten, thereby forming a metal composite hydroxide (Ni_{0.795}Co_{0.05}Mn_{0.15}W_{0.005}(OH)₂).

The formed metal composite hydroxide (Ni_{0.795}Co_{0.05}Mn_{0.15}W_{0.005}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni_{0.795}Co_{0.05}Mn_{0.15}W_{0.005}(OH)₂) and lithium hydroxide

(LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 770° C. for 15 hours to fabricate positive active material (LiNi_{0.795}Co_{0.05}Mn_{0.15}W_{0.005}O₂) powder according to an embodiment 14.

Fabrication of Positive Active Material According to Comparative Example 7

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A first base aqueous solution including nickel sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:manganese=98:2) and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 5 hours to 15 hours while mixing a second base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=80:8:12) with the first base aqueous solution at 0.561 liter/hour. In addition, continuously, the first base aqueous solution and the 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 10 hours to 20 hours while mixing a third base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=72:6:22) with the first and second base aqueous solutions at 0.561 liter/hour. In addition, a sodium hydroxide solution was supplied to adjust a pH.

A formed metal composite hydroxide (Ni_{0.80}Co_{0.05}Mn_{0.15}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni_{0.80}Co_{0.05}Mn_{0.15}(OH)₂) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 770° C. for 15 hours to fabricate positive active material (LiNi_{0.80}Co_{0.05}Mn_{0.15}O₂) powder according to a comparative example 7.

FIG. 33 is a graph showing an atomic ratio of the positive active material according to the comparative example 7, FIG. 34 is a graph showing an atomic ratio of the positive active material according to the embodiment 14 of the inventive concepts, and FIG. 35 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 14 of the inventive concepts and the comparative example 7.

Referring to FIGS. 33 and 34, atomic ratios of the positive active materials according to the comparative example 7 and the embodiment 14 were measured as shown in FIGS. 33 and 34 and the following tables 14 and 15.

TABLE 14

	Center	Surface
Ni	88.0	73.1
Co	5.3	5.9
Mn	6.7	21.0

TABLE 15

	Center	Surface
Ni	86.4	73.6
Co	5.9	5.6
Mn	7.2	20.3
W	0.5	0.5

As shown in FIGS. 33 and 34 and the tables 14 and 15, nickel, cobalt and manganese have concentration gradients in at least a portion of a particle in a direction from a center toward a surface of the particle. On the contrary, a concentration of tungsten corresponding to the additive metal is substantially constant in the whole of the particle.

Referring to FIG. 35, half cells were manufactured using the positive active materials according to the embodiment 14 and the comparative example 7, and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C.

As shown in FIG. 35, capacity and charge/discharge characteristics of the embodiment 14 doped with the additive metal are superior to those of the comparative example 7 not doped with the additive metal.

Fabrication of Positive Active Material According to Embodiment 15

WO₃ powder was dissolved at a concentration of 0.24M in 0.4 L of a 1.5M lithium hydroxide solution. The formed solution was dissolved in 9.6 L of a 4M sodium hydroxide solution to form 10 L of an additive aqueous solution in which tungsten (W) was dissolved.

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A first base aqueous solution including 2M nickel sulfate and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 15 hours to 25 hours to form a core portion.

In addition, subsequently, a second base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=80:10:10) was continuously provided into the reactor for a time of 5 hours to 10 hours to form a shell portion. In addition, the additive aqueous solution was supplied into the reactor to adjust a pH and to add tungsten during the formation of the core portion and the shell portion, and thus a metal composite hydroxide (Ni_{0.945}Co_{0.025}Mn_{0.025}W_{0.005}(OH)₂) was formed.

The formed metal composite hydroxide (Ni_{0.945}Co_{0.025}Mn_{0.025}W_{0.005}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni_{0.945}Co_{0.025}Mn_{0.025}W_{0.005}(OH)₂) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 750° C. for 10 hours to fabricate positive active material (LiNi_{0.945}Co_{0.025}Mn_{0.025}W_{0.005}O₂) powder according to an embodiment 15.

Fabrication of Positive Active Material According to Comparative Example 8

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. A first base aqueous solution including 2M nickel sulfate and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, for a time of 15 hours to 25 hours to form a core portion.

In addition, subsequently, a second base aqueous solution including nickel sulfate, cobalt sulfate and manganese sulfate (concentration: 2M, molar ratio of nickel:cobalt:manganese=80:10:10) was continuously provided into the reactor for a time of 5 hours to 10 hours to form a shell portion. In addition, a sodium hydroxide solution was supplied to adjust a pH during the formation of the core portion and the shell portion.

A formed metal composite hydroxide (Ni_{0.95}Co_{0.025}Mn_{0.025}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide (Ni_{0.95}Co_{0.025}Mn_{0.025}(OH)₂) and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 700° C. for 10 hours to fabricate positive active material (LiNi_{0.95}Co_{0.025}Mn_{0.025}O₂) powder according to a comparative example 8.

FIG. 36 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 15 of the inventive concepts and the comparative example 8.

Referring to FIG. 36, half cells were manufactured using the positive active materials according to the embodiment 15 and the comparative example 8, and discharge capacities according to the number of charge/discharge cycles of the half cells were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C.

As shown in FIG. 36, capacity and charge/discharge characteristics of the embodiment 15 doped with the additive metal are superior to those of the comparative example 8 not doped with the additive metal.

Fabrication of Positive Active Material According to Embodiment 16

WO₃ powder was dissolved at a concentration of 0.47M in 0.4 L of a 1.5M lithium hydroxide solution. The formed solution was dissolved in 9.6 L of a 4M sodium hydroxide solution to form 10 L of a first additive metal aqueous solution in which tungsten (W) was dissolved.

Na₂MoO₄ powder was dissolved at a concentration of 0.019M in 10 L of a 4M sodium hydroxide solution to form 10 L of a second additive metal aqueous solution in which molybdenum (Mo) was dissolved.

10 liters of distilled water was provided into a coprecipitation reactor (capacity: 40 L, output power of rotary motor: 750 W or more). Thereafter, a N₂ gas was supplied into the reactor at a rate of 6 liter/min, and the distilled water was stirred at 350 rpm while maintaining a temperature of the reactor at 45° C. For a time of 15 hours to 25 hours, a 2M nickel sulfate aqueous solution and a 10.5M ammonia solution were continuously provided into the reactor at 0.561 liter/hour and 0.128 liter/hour, respectively, and the second additive metal aqueous solution was continuously

provided into the reactor for adjustment of a pH and Mo-doping. Thus, a core portion was formed.

After the formation of the core portion, the 2M nickel sulfate aqueous solution and the 10.5M ammonia solution were continuously provided at 0.561 liter/hour and 0.128 liter/hour, respectively, and the first additive metal aqueous solution was continuously provided for adjustment of the pH and W-doping, for a time of 5 hours to 10 hours. Thus, a shell portion was formed.

A formed metal composite hydroxide (Ni_{0.99}W_{0.005}Mo_{0.005}(OH)₂) was filtered, was cleaned by water, and then, was dried in a vacuum dryer at 110° C. for 12 hours. After the metal composite hydroxide and lithium hydroxide (LiOH) were mixed with each other at a molar ratio of 1:1, the mixture was heated at a heating rate of 2° C./min and then was maintained at 450° C. for 5 hours to perform a preliminary firing process. Thereafter, the mixture was fired at 770° C. for 10 hours to fabricate positive active material (LiNi_{0.99}W_{0.005}Mo_{0.005}O₂) powder according to an embodiment 16.

FIG. 37 is a graph showing an atomic ratio of a positive active material precursor according to the embodiment 16 of the inventive concepts, and FIG. 38 is a graph showing an atomic ratio of a positive active material according to the embodiment 16 of the inventive concepts. FIG. 39 is a graph showing charge/discharge characteristics of the positive active materials according to the embodiment 16 of the inventive concepts and the comparative example 1, and FIG. 40 is a graph showing capacity retention characteristics of the positive active materials according to the embodiment 16 of the inventive concepts and the comparative example 1.

As described above, the metal composite hydroxide (Ni_{0.99}W_{0.005}Mo_{0.005}(OH)₂) was formed as a positive active material precursor according to the embodiment 16, and an atomic ratio thereof was measured as shown in FIG. 37 and the following table 16.

TABLE 16

	0 μm	2.0 μm	4.0 μm	5.0 μm
Ni	99.17	99.01	98.84	99.00
Mo	0.83	0.95	0.63	0.02
W	—	0.04	0.53	0.98

In addition, an atomic ratio of the positive active material (LiNi_{0.99}W_{0.005}Mo_{0.005}O₂) according to the embodiment 16 was measured as shown in FIG. 38 and the following table 17.

TABLE 17

	0 μm	2.0 μm	4.0 μm	5.0 μm
Ni	99.45	99.40	99.37	99.28
Mo	0.23	0.26	0.30	0.21
W	0.32	0.33	0.33	0.51

In addition, a half cell was manufactured using the positive active material according to the embodiment 16. Discharge capacities of the half cell were measured under conditions of cut off 2.7V to 4.3V, 0.1 C, and 30° C., and discharge capacities according to the number of charge/discharge cycles of the half cell were measured under conditions of cut off 2.7V to 4.3V, 0.5 C, and 30° C. The measured results of the embodiment 16 were compared with those of the half cell manufactured using the positive active material according to the comparative example 1. The compared results are shown in FIGS. 39 and 40 and the following table 18.

TABLE 18

	0.1 C, 1st Dis- Capa (mAh/g)	1st Efficiency	0.2 C Capacity (mAh/g)	0.2/0.1 C	0.5 C Capacity (mAh/g)	0.5 C/ 0.1 C	cycle	0.5 C Cycle Retention	L/L (mg/cm ²)
Comparative example 1	247.5	96.8%	242.3	97.9%	232.5	93.9%	100	73.7%	6.52
Embodiment 16	248.3	95.8	245.2	98.7	239.2	96.3	100	85.0	6.01

As shown in FIGS. 39 and 40 and the table 18, capacity and charge/discharge characteristics of the embodiment 16 doped with the additive metal are superior to those of the comparative example 1 not doped with the additive metal.

The positive active material and the method of fabricating the same according to the embodiments of the inventive concepts may be applied to a lithium secondary battery and a method of manufacturing the same. The lithium secondary battery including the positive active material according to the embodiments of the inventive concepts may be used in various industrial fields such as portable mobile devices, electric cars, and energy storage systems (ESS).

The positive active material according to the embodiments of the inventive concepts may include lithium, an additive metal, and at least one of nickel, cobalt, manganese, or aluminum. A concentration of at least one of nickel, cobalt, manganese, or aluminum may be changed in a particle. The additive metal may include an element different from nickel, cobalt, manganese, and aluminum, and an average content of the additive metal (e.g., tungsten) may be less than 2 mol %. Thus, it is possible to realize or provide the positive active material which has high capacity, long life span, improved thermal stability, and high reliability.

While the inventive concepts have been described with reference to exemplary embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made without departing from the spirits and scopes of the inventive concepts. Therefore, it should be understood that the above embodiments are not limiting, but illustrative. Thus, the scopes of the inventive concepts are to be determined by the broadest permissible interpretation of the following claims and their equivalents, and shall not be restricted or limited by the foregoing description.

What is claimed is:

1. A positive active material comprising:

- (i) lithium,
- (ii) an additive metal, and
- (iii) at least one of nickel, cobalt, manganese, or aluminum,

wherein the additive metal includes an element different from nickel, cobalt, manganese, and aluminum, wherein an average content of the additive metal is less than 2 mol %,

wherein a concentration of at least one of nickel, cobalt, manganese, or aluminum is changed in a particle, wherein the particle comprises an inner portion relatively adjacent to a center of the particle and an outer portion relatively adjacent to a surface of the particle,

wherein the positive active material includes a first crystal structure and a second crystal structure, which have different crystal systems from each other

wherein a ratio of the first crystal structure is higher than a ratio of the second crystal structure in the outer

portion, and the ratio of the second crystal structure is higher than the ratio of the first crystal structure in the inner portion,

wherein the first crystal structure is a cubic crystal structure, and

wherein the second crystal structure is a trigonal or rhombohedral crystal structure.

2. The positive active material of claim 1, wherein at least one of nickel, cobalt, manganese, or aluminum has a concentration gradient in a whole of the particle.

3. The positive active material of claim 1, wherein the additive metal has a substantially constant concentration in a whole of the particle.

4. The positive active material of claim 1, wherein at least one of nickel, cobalt, manganese, or aluminum has a concentration gradient in one of the inner portion and the outer portion, and

wherein a concentration of at least one of nickel, cobalt, manganese, or aluminum is substantially constant in the other of the inner portion and the outer portion.

5. The positive active material of claim 1, wherein a concentration gradient of at least one of nickel, cobalt, manganese, or aluminum is changed in the particle.

6. The positive active material of claim 1, wherein the additive metal includes at least one of tungsten, molybdenum, zirconium, niobium, tantalum, titanium, rubidium, bismuth, magnesium, zinc, gallium, vanadium, chromium, calcium, strontium, or tin.

7. The positive active material of claim 1, wherein the outer portion surrounds at least a portion of the inner portion.

8. The positive active material of claim 1, wherein the positive active material comprises:

primary particles; and
a secondary particle in which the primary particles are aggregated,

wherein at least one of the primary particles includes both the first crystal structure and the second crystal structure.

9. The positive active material of claim 8, wherein the primary particle including both the first crystal structure and the second crystal structure is provided at a boundary of outer portion and the inner portion.

10. A method of fabricating a positive active material, the method comprising:

preparing: a first base aqueous solution which includes at least one of nickel, cobalt, manganese or aluminum; a second base aqueous solution of which a concentration of at least one of nickel, cobalt, manganese or aluminum is different from that of the first base aqueous solution; and an additive aqueous solution including an additive metal;

providing the first base aqueous solution, the second base aqueous solution and the additive aqueous solution into

31

a reactor and adjusting a ratio of the first and second base aqueous solutions, thereby fabricating a positive active material precursor in which a metal hydroxide including at least one of nickel, cobalt, manganese, or aluminum is doped with the additive metal; and
 firing the positive active material precursor and lithium salt to fabricate a positive active material in which a metal oxide including lithium and at least one of nickel, cobalt, manganese or aluminum is doped with the additive metal, wherein a doping concentration of the additive metal is less than 2 mol %,
 wherein a concentration of at least one of nickel, cobalt, manganese or aluminum is changed in a particle of the positive active material precursor,
 wherein the particle comprises an inner portion relatively adjacent to a center of the particle and an outer portion relatively adjacent to a surface of the particle,

32

wherein the positive active material includes a first crystal structure and a second crystal structure, which have different crystal systems from each other

wherein a ratio of the first crystal structure is higher than a ratio of the second crystal structure in the outer portion, and the ratio of the second crystal structure is higher than the ratio of the first crystal structure in the inner portion,

wherein the first crystal structure is a cubic crystal structure, and

wherein the second crystal structure is a trigonal or rhombohedral crystal structure.

11. The method of claim **10**, wherein a firing temperature of the positive active material precursor and the lithium salt is adjusted depending on the doping concentration of the additive metal.

* * * * *